High Temperature Superconductivity

Promise and Prospects

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Preface

This volume has been put together by the Tata Energy Research Institute, since the promise held by future developments in the science and technology of superconductivity has been the subject of much debate in the last two or three years. While assessments of the future impact of innovations in this field have ranged from extreme excitement to guarded pessimism, the staff of the Tata Energy Research Institute felt that a continuing appraisal of developments in superconductivity would be beneficial not only in disseminating useful technical information on the subject, but would also serve the larger purpose of informing policymakers and the public about the overall potential and likely implications of technological changes that would take place in this area of scientific endeavour. While no alterations in investment plans are likely to take place resulting from predictions on possible future developments in this field (as is the case with investments in computer hardware, for instance, wherein the rate of technical innovation is almost breathtaking), it is important for a society which relies more and more on science to be aware of future developments in vital areas of scientific research. Even more important is the fact that today large-scale funding is being provided for research in this area, and the question of priorities in funding of research and development has to be answered in relation to predictions of future benefits, however uncertain and probabalistic they may be.

The history of the space programme in the world shows how a particular mission when first conceived of and launched can greatly underestimate the spin-off benefits that come from achievements over time. Indeed, space technology has revolutionalised telecommunications, the science of assessment of natural resources, predictions of weather and climate changes, all of which would have far-reaching implications for all the actions of the human race.

The utilisation of these benefits invariably takes place with substantial lags in time and, therefore, when a programme of scientific development is launched, one merely sees the tip of the iceberg and it is only later that a whole range of options in which subsequent innovations can be fruitfully applied become apparent. Perhaps this is the case with superconductivity as well. On the other hand, there is the possibility of overimaginative scenarios ranging close to science fiction-type predictions that could truly direct scarce resources into scientific endeavour which may in the end prove to be non-viable and unproductive. There are some who feel this is the case with research on superconductivity as well.

This volume attempts to provide various points of view and to mix scientific detail with policy analysis. The Tata Energy Research Institute is a non-profit research institution and the dissemination of scientific information has been one of our most important concerns. Hence, while this book may not answer many questions, it perhaps would result in the right questions being asked. This would give us adequate satisfaction and perhaps a basis for structuring the next volume in this series which we hope will follow in about two years.

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Superconductivity and world electricity use

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Abstract

This article deals with the possible impacts of the new superconducting materials on their future applications and their effects on world electricity use. An optimistic viewpoint has been presented on the capabilities of scientists and technologists being able to circumvent the current problems associated with these applications.

The discovery of what may be termed "high temperature superconductivity" (HTSC) in early 1987 generated great excitement and began a worldwide race to exploit the new phenomenon that is still continuing. For those not familiar with the technical aspects of HTSC, the following very brief summary is provided.

The phenomenon of superconductivity has long been known and, indeed, used on a limited scale. The term refers to the total absence of resistance to the flow of electricity in a conductor. Until the recent discoveries, it could be created in certain metals or alloys only at temperatures close to absolute zero (-273°C), temperatures that could be maintained only in a bath of liquid helium. Each of the factors involved was itself costly, and together they made the practical use of superconductivity almost prohibitively expensive. Helium is a relatively scarce element that is expensive to produce. it is expensive to liquefy, since the liquefaction occurs at close to absolute zero. The maintenance of helium in the liquid state is also expensive because of the need for large refrigeration capacity to attain and maintain the necessary low temperatures. As a result, superconductivity remained a tool for experimental physics; its commercial application was limited almost exclusively to certain medical imaging devices with performance so superior to alternative imaging (e.g., X-rays) that it justified the very high cost.

The 1987 discoveries demonstrated conclusively that superconductivity was possible at higher temperatures than had heretofore been thought possible. This improvement in absolute terms was not very great--less than 100°C, and -173°C is still a very low temperature. The significance of the improvement, however, was that superconductivity could be attained at temperatures above -196°C, the temperature at which nitrogen liquefies. Far from being rare, nitrogen is the most abundant gaseous element. It is far easier to liquefy and handle, and costs two orders of magnitude less than helium. There is an abundance of industrial experience with it consuming many millions of liters a year. Thus, with liquid nitrogen cooling, for the first time it makes sense to consider the commercial applications of superconductivity.

For all its attractiveness, HTSC is not practical in every use of electricity. It makes no sense to apply it to electric lighting, or in small electric motors, which exist in the hundreds of millions throughout the world. Initially, at least, attempts to apply it commercially will be focused on electrical devices that involve a magnetic field, because of the special advantage superconductivity gives to electromagnets. An electromagnet consists of an iron core surrounded by wire windings; the passage of current through the windings generating a magnetic field. The advantage of HTSC is that it allows the production of the desired magnetic field strength with far greater efficiency and with smaller bulk. This is because at ordinary temperatures the resistance of the wire to the electric current produces heat. The heat constitutes lost energy, and in designing for ultra-high magnetic field strength puts a practical limit on size due to the buildup of heat. With HTSC there is great improvement in efficiency and another order of magnitude in attainable field strength.

The limitation to magnetic applications still leaves a wide range of possibilities, since all electric motors contain magnets and essentially all electricity generation involves their use. The need for refrigeration to maintain the liquid nitrogen, on the other hand, rules out the use of HTSC in all but the largest motors. Such motors, by virtue of their size, use large quantities of electricity; thus even a relatively small gain in efficiency coupled with a reduction in size could more than offset the liquid nitrogen costs. In generation, most units are large in either relative or absolute terms and again, small gains in efficiency and size reduction can be worth the extra cost of HTSC.

HTSC also offers advantages in the exotic techniques of electricity generation, magnetohydrodynamics (MHD) and nuclear fusion. Here the gain is in the ability to produce ultra-high strength magnetic fields. In the former instance a given flow of ionized gas through a stronger field yields greater output; in the latter instance the stronger field makes it easier to contain the fusion fuel so that fusion can occur.

The ability to produce high strength magnetic fields more efficiently also holds promise in two applications in transportation. One is in magnetically levitated (maglev) rail transportation. Maglev transportation uses magnetic repulsion to lift and hold a train a short distance above the track, thus eliminating traction resistance and leaving only wind resistance to be overcome in moving the train forward. The second transportation instance, surprising, is in magnetic ship propulsion. Here there are no moving parts. A superconducting magnet creates an onboard magnetic field while the surrounding water is charged with an electric current from the ship. The current creates its own magnetic field and the reaction between the two fields drives the ship forward.

Conventional propeller drive is ;subject to an inherent limitation in the speed with which it can move a ship. Above a certain propeller speed the energy of the revolving propeller is diverted into the phenomenon known as cavitation, the rapid formation and collapse of vapor pockets in the water, which damages the propeller. With the propeller eliminated, far higher speeds are attainable, at least in theory. Even at conventional speeds, however, HTSC offers the advantage of drastically reducing the weight of the propulsive equipment--weight that can be in the form of cargo instead.

As noted earlier, "conventional" superconductivity is already being applied in medical imaging with the use of the phenomenon known as nuclear magnetic resonance. Without getting into technical detail, suffice it to say that technique yields images of the interior of the body that approach the quality of photographs. The true significance, however, is not so much the improved image quality, although that is certainly important. Rather, it transcends the limitations of X-rays in obtaining interior images. With magnetic resonance, detailed images of soft tissues are obtainable, far beyond the capability of radiography, with consequent enormous benefits in medical diagnosis. Small wonder that this technique is in use despite the high cost of helium cooling.

A totally new medical technique is in the offing through the use of a device known as a SQUID (Superconducting Quantum Interface Device). A SQUID is capable of detecting extremely weak magnetic fields, such as those in the human brain and heart. New opportunities for diagnosis are thus opened up--possible before at very high cost, now available at reasonable cost.

Yet another application in the production of magnetic fields is in magnetic separation. Ordinary electromagnets have long been used in the processing of coal and other mineral raw materials to remove impurities. By passing a stream of material through a magnetic field, the magnetically susceptible components of the stream can be diverted and collected. With ultrahigh strength fields, this technique can be applied to other processes heretofore impossibly expensive, such as the removal of nitrogen and sulfur oxides from stack gases, the removal of toxic metals from water and the recovery of metallic catalysts from chemical reactors.

In addition to the foregoing application, all of which involve magnetic fields, there are two others of potential importance which make use of the superconductivity itself, that is, the disappearance of electrical resistance. The first is in electricity transmission. In a modern electric grid, some 10 percent of the energy is lost between the generator and the point of consumption. Some of this loss is in the transformers that raise and lower the voltage, but most is due to the resistance in the transmission and distribution lines. The loss is most acute in transmission because this is where the power flows are concentrated.

Superconducting transmission would use a superconductor inside an insulated pipe filled with liquid nitrogen. There would be no need for the conventional transmission towers, which are essentially a substitution for insulation. The transmission lines of today are suspended from towers only because it is cheaper to use the surrounding air as insulation than to use the alternative means of burying the line and surround it with the necessary insulating material. (This is, of course, done in metropolitan centres, but only because it is either required by law or would be still more expensive to acquire the rights of way and make the necessary physical configurations to avoid danger to the public. The superconducting line would be only thermal insulation to keep the nitrogen liquid, since with no resistance[1] there is no need for a voltage to "push" the electricity through the conductor. Thus it would be no larger in diameter than today's buried transmission lines, and because of the greater carrying capacity of the superconductor, could well be of smaller diameter even with the insulation.

Another application in the operation of an electric grid is electricity storage. If a superconductor is formed into a ring and a current is introduced, the current, once started, will literally flow forever as long as the superconducting state is maintained. One of the troublesome features of electricity consumption is its daily variability. During the day, when most human activity takes place electricity use is high; at night, when most people are sleeping and most factories are shut down, electricity use falls to a low. In cold climates where electric space heating is common the peak daily use may occur at night; in warm climates where air conditioning is common, the peak during daylight hours is accentuated.

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[1] Actually, the resistance with alternating current is not zero, but close to it.

Providing for this daily fluctuation is costly, since it requires generating capacity that is used for only a short time (the sharper the daily peak, the shorter the time). Such capacity is economically inefficient; for it must be paid for even though it is not producing. In some countries this fluctuation is dealt with at the consuming end. Electricity used for heat is stored in the form of ice. The common means of storage, however, is pumped storage. In this technique electricity is used in off-peak periods to pump water from a lower reservoir to a higher one. During the time of peak use the water flows back down to the lower reservoir, generating power. Unfortunately, this involves considerable energy loss. One kilowatt-hour is lost for every two produced in this manner.

The superconducting ring as an energy storage device offers the highly attractive advantage of 100 per cent efficiency (something almost never attained in the real world in any process or activity). It can be of any size and can be located anywhere. With the use of such storage rings not only could the daily load fluctuation be handled at far lower cost, the flexibility of grid management in general would be enhanced.

The final application to be mentioned here is in electronics, in communications and computing equipment. The use of superconducting materials as coatings in such things as radiowave generators, resonators and wave guides could extend the use of the electromagnetic spectrum to frequencies heretofore unobtainable for commercial use. The usable spectrum could be increased sensitivity that would accompany the use of such coatings, satellite dishes could be reduced to a few inches in diameter, and television could achieve photographic quality. The introduction of HTSC into semiconductor technology will provide yet another advance in computing speed and reduction in size of components. The latter will be possible through the breaking of the "heat barrier" that is currently hampering efforts to further reduce size. Even with the minuscule currents present in computers, the cramming of more and more circuits and components on a single integrated chip has raised problems in conducting away the heat generated by the resistance. With no resistance, no heat is generated.

Research and development on all these applications is proceeding at an almost frantic pace around the world as companies and countries strive to achieve the commercial advantage of being the first with practicable and workable devices and equipment. Maglev transportation was on the verge of commercial introduction even before the discovery of HTSC, notably in Germany and Japan. The

Germans are sticking with nonsuperconductive magnets, but the Japanese are working with superconductivity. The Japanese have also built and operated a magnetically propelled ship superconducting generators and motors are being investigated. In the United States an experimental superconducting storage ring has been successfully operated, as has a superconducting transmission line.

All of this, however, has been with conventional technology--that is, with the use of helium cooling. This is because the materials that exhibit superconductivity at liquid helium temperatures can be fabricated into wire. The new HTSC materials, in contrast, suffer from a formidable disadvantage: they are ceramics, hence brittle and not capable of being drawn into wire. The unfortunate circumstance is that as things now stand, the HTSC that can be readily achieved in the laboratory cannot yet be translated into commercial use. An equally formidable problem is that the HTSC materials so far discovered suffer from severe limitations in current carrying capacity (again, something that is far less a problem with the conventional superconducting materials). Every superconducting material has a property known as the critical current density, at which the magnetic field produced by the current itself destroys the superconductivity. This is not a problem with electronic applications, with their small currents that can be carried in coatings rather than wire. Where the current density is high, it can be lowered by increasing the cross section of the conductor, but then one is no longer dealing with wire, so magnet windings are impossible. There is also the matter of chemical stability. The HTSC compounds tend to deteriorate in the presence of oxygen or moisture.

These problems have led some observers to conclude that the prospects for widespread and large-scale application of HTSC are dim at best. This view, however, ignores or unduly derogates the demonstrated capacity of today's science and technology to overcome seemingly insuperable obstacles. The entire semiconductor industry of the world, for example, developed in the face of seemingly impossible problems of purity and the need for the deliberate manipulation of impurities at levels far beyond what had previously been achieved. Not only were the necessary techniques developed in the laboratory, they were translated into commercial processes that now routinely process tons of materials with fantastic precision. Another example is optical fibres, where the initial limitations on transparency have been overcome to the point where, if such glass filled the Mariana Trench (at more than 10 kilometers, the deepest spot on the world's oceans), an observer at the surface would be able to see the bottom.

There is also reason for optimism in the motivation behind the current research and development. It has gone beyond the satisfaction of scientific curiosity to the far stronger spur of profit possibilities. Given this combination of motive and competence, it is not unreasonable to expect that if suitable materials exist and the necessary processing and fabrication techniques are at all possible, they will be discovered and perfected. The real question is the timing. On this point, given the short time since the initial discoveries, nothing can be said beyond the near certainty that the first commercial applications of HTSC in electronics will appear within a few years.

Ignoring the timing, what would a world be like with HTSC in ubiquitous use, as the transistor is today? One thing can be said with confidence. Although HTSC generation for a given level of consumption, this efficiency gain will be swamped by the increased electricity use accompanying all other HTSC applications. They all will require liquid nitrogen refrigeration. As for how everyday will be transformed, it is likely that it will be in ways that cannot be conceived of at present, just as it was impossible to foresee the impact of the transistor on life almost everywhere in the world. The transistor radio is found everywhere, not just in the high income developed countries. To give only one example of an ultimate consequence that is conceivable today, consider magnetic levitation. it is in principle possible to design a portable levitation device, about the size and capability of a fork lift, that could be used anywhere a metal trackway could be installed. this could be applied not only to materials handling in factories, but in dock and assembly areas anywhere in the world. Individual workers could thus move large quantities of materials by merely pushing levitated pallets with self contained, battery powered nitrogen refrigerators. The important point is that although HTSC production and fabrication will involve high technology, just as semiconductors and electronic devices do today, the *use* of such devices in their applications will not be limited to the developed or developing countries. The opportunity is there for all countries to benefit.

This discussion would not be complete without mention of the truly revolutionary possibility that has been suggested by the recent discoveries. That possibility is superconductivity at far higher temperatures, even room temperature. Any increase in the transition temperature at which superconductivity occurs would be helpful, since the further that temperature is above the -196° liquid nitrogen temperature, the better the performance of the superconducting material. Room temperature superconductivity, however, would be something entirely different. There would be no need for refrigeration, thus no limitation on applications. Experiments since the original discoveries have repeatedly hinted at the occurrence of superconductivity at room temperature., The phenomenon has been evanescent, however, and not repeatable. If it is actually taking place, it seems to occur in materials that are not stable--they do not retain a given set of properties over time.

Research is continuing in an effort to pin down the phenomenon, to find out whether it is really occurring. If it can be demonstrated conclusively that there is such a thing as room temperature superconductivity, the possibilities are so immense that the effort to get the phenomenon out of the laboratory into commercial application would dwarf the effort by the United States government during World War II to develop the nuclear fission phenomenon into a military weapon.

The ability with RTSC (room temperature superconductivity) to design superefficient generators and motors, to transmit an distribute electricity with no losses, to design superelectromagnets constrained only by material strength rather than power consumption--all of this constitutes a vista of unparalleled scope. It is beyond the imagination to attempt to specify the ways in which electricity generation, distribution and use would change, and the effect this would have on the world's inhabitants. It would be comparable to the invention of the steam engine, which made motive power possible and freed societies from dependence on water-power as the only alternative to animal or human labour. With such possibilities being hinted at by some of the experiments, little wonder the search is being pursued with such intensity.

Initial reflections on the energy-saving implications of advances in high-temperature superconductivity

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Abstract

An analysis of the future implications on energy savings due to large scale applications of superconductors has been presented. No significant energy saving potential from the various envisaged applications of these superconducting materials is apparent at present. At present levels of technolgy larger energy savings potential exists by use of conventional means which would be easier technically to incorporate and disseminate than these frontline means such as superconductors.

Introduction

This chapter is a preliminary effort to lend perspective to the potential of high-temperature superconductivity (here called HTSC) to save energy. No effort is made here to analyze the science, engineering, or economics of practical HTSC devices. Rather, the heroic (but possibly, in the end, valid) assumption is made, arguendo, that HTSC devices of any reasonably desired qualities can be made at affordable cost: i.e., that all constraints of flux density, fabricability, durability, economics, etc. simply disappear. For convenience, one could even assume, even more heroically, that this is achieved at ambient rather than at liquid-nitrogen temperature (assuming this to be physically possible, which is unclear at this writing). Should this in fact occur, then, would it open important new opportunities for the more efficient generation and use of electric energy?

The line of thinking set out below suggests that the potential energy savings, though not trivial, are unimportant compared with those which in no way rely on superconductivity and which are already commercially available, practical, and highly cost-effective. The initial conclusion explored here is that except in fast, high-density computers and electronics, and perhaps in some thermal applications[1], the practical consequence of HTSC is likely to be much less than than meets the eye.

Electric power transmission

In most industrialized countries, losses in high-voltage transmission lines are currently a few percent of energy transmitted (whereas losses in the far larger length of distribution circuit range from as large to twice as large). A few percent of 2.4 TW-h/y -- the total electric usage in, for example, the United States -- is worth perhaps $4 billion/y retail or $2 billion/y wholesale: not trivial. (Neither would be the task of reconductoring; the U.S. has some 1 million circuit-km of transmission lines, about a fifth of it >189 kV.) Under sufficiently heroic cost assumptions, this saving could be worth pursuing, at least in incremental expansions and replacements of the existing grid. In general, if technical requirements (including reliability and mechanical strength) can be satisfied, the basic economic question will be whether the considerable cost of reconductoring -- and, if the operation is at less than ambient tempeature, continuous cooling, presumably requiring underground rather than aerial siting -- can be justified by the few percent power savings.

Bulk power transmission, however, is not limited by line losses, but rather by cost, siting, and stability. HTSC lines would eliminate resistive losses at the cost not only of money but also, most likely, of grid stability, since the lines' impedance would become pure reactance. While HTSC windings which could aso be used in the electric generators or alternators would compensate in part by increasing the rotors' effective angular momentum, it is far from clear that the more reactive grid would not, in net effect, exacerbate already troublesome stability problems. (In some significant cases it is not even known whether these problems necessarily have a control-theoretic solution.) If we had HTSC transmission lines today, it seems doubtful that they would permit, save in a few special cases, moving more power around.

Nor should we want to, because (a) bulk power transmission is far too vulnerable to accidental or deliberate disruption[2], (b) many disagreeable surprises are emerging in the subtle biological effects of both AC and DC high-voltage transmission lines[3], and (c) as will be suggested below, it is generally cheaper to save the power than to transmit it, even if making it were free. Saved electricity requires no transmission; it is already where it's wanted.

It is possible that this view of the limited likely net benefits of HTSC bulk power transmission might change in a country, such as the USSR, which has very high (~20-30+%) grid losses. In such cases, however, the very long haul lengths would also presumably exacerbate the problems of cost, grid stability, and vulnerability.

Motors

HTSC could in principle eliminate I^2R (resistive) losses in motor windings. These are typically about half of total losses in large, fully loaded induction motors (less at part load). Other losses -- friction, windage, magnetic core losses, stray load losses -- would probably be unaffected. Total losses are only on the order of one-tenth of motors' electric use, which in U.S. industry averages about 140 GW. Eliminating all I^2R losses in U.S. industrial motors would thus save on the order of 7 GW. While again a worthy goal -- more than $10 billion worth of capacity and ~$1b/y in fuel costs, albeit at a considerable potential cost in motor conversions -- other improvements already proven and available for industrial motors and their controls and drivetrains can save approximately ten times that much: in U.S. industrial motors, about 70 GW at average costs of approximately 0.3-0.5 US cents per kW-h saved[4].

Electric storage

Superconductive storage has recently been successfully demonstrated in a practical utility environment in the Pacific Northwest, and is currently being commercialized on a modest unit scale. HTSC storage may offer some economic advantages over other means of bulk power storage. However, probably everything that can be done with HTSC storage (bulk or dispersed) could instead be done more cheaply with end-use efficiency and load management.

At first glance one might suppose that HTSC storage could make electric cars competitive with efficient liquid-fueled cars (which in principle always beat chemical-battery cars). While the author has not yet analyzed this question in detail, it currently appears reasonable to accept General Motors Corporation's conclusion that it is thermodynamically and economically better to burn fuel directly in an efficient car (perhaps a fuel-cell or an internal-combustion-engine series hybrid) than to burn it in a power plant to make electricity to run an electric car using any kind of onboard storage, including HTSC. Thus it seems prima facie unlikely that HTSC would produce a flood of electric cars -- although if it did, it would increase electricity use by substantially less than other, non-HTSC-related electric savings would reduce it[5].

HTSC-levitated rail vehicles

HTSC-based levitated rail systems ("maglev" technology, already demonstrated at liquid-helium temperature in Japan) are probably a sound idea for high-density fixed corridors. However, rail travel doesn't use much energy anyway -- 0.2% of total US electric sales, and no more than a few percent in even the most rail-intensive countries. Railways are also already very energy-efficient: what maglev could in principle eliminate (the friction of steel wheels on steel rails and in bearings) is an unimportant loss factor. Maglev does not solve problems of corridor siting, cost, or air resistance -- the real constraints on rail travel and its energy use. In other transport modes, too, GM's plausible view is that whatever HTSC might do can be done about as well without it.

Magnetic levitation of goods

Directly levitating certain goods, or pallets or trays containing them, would suffer from the same basic objection as maglev rail, namely that essentially the same benefits, to the extent they're worth pursuing, are available without HTSC. True, maglev could permit switching of goods packets between branches of a large (and extremely costly) conduit network, somewhat like a giant pneumatic message-tube system, but the same thing can be done with wheels of various kinds. Wheels, while perhaps old-fashioned, are hardly very inefficient. And there are many other interesting ways to do door-to-door freight. To mention two: (a) GM does <24-h door-to-door shipments from the Flint area to the Atlanta and Kansas City areas in a "Roadrailer" vehicle which converts in seconds between a heavy-lorry trailer and a railway freight waggon, or back again. Its tight couplings and air suspension in the unit-train configuration eliminate unauthorized access and jerks on acceleration and deceleration: it is claimed that a cup of water set on the outside sill will still be sitting there at destination. The energy saving is about 75%, and the payback is excellent just from avoided demurrage and just-in-time inventory of major car components. (b) Containerized airships continue to offer considerable promise. A few years ago, Lucas Aerospace developed a version that could hover in a strong wind with no mooring tower, stabilized by Harrier jet thrusters, although its noise and economics remain uncertain.

Very strong magnets

Large magnets have uses like railguns, metal-forming, particle accelerators, and magnetic-resonance imaging (though the last of these might fall from favour as we discover unexpected biological effects of multitesla DC fields). No doubt the military- and medical-industrial complexes can be relied upon to bring such applications to market. Their net effect will probably be to reduce electric use. (Extremely powerful small motors already exist too, using RE-Fe-B non-superconducting magnets; HTSC motors would be even stronger and smaller, but their benefits seem incremental.)

Soviet researchers have devoted considerable attention to possible magnetohydrodynamic applications of large HTSC magnets, and have made impressive progress in the engineering of both MHD and Tokomak-fusion magnets[6]. It is not clear, however, that the larger research projects of which these efforts are a part will lead in a promising direction.

For example, John Holdren at Berkeley reports that according to an elaborate two-year U.S. Department of Energy study on fusion cost, successful HTSC might have two cost effects on controlled fusion. If it merely cuts the cost of liquid-helium refrigeration (say to zero) without changing basic design of the machine, it would reduce busbar electric cost by of order 3%. If, on the other hand, it permits a much smaller fusion machine per GW, then the maximum possible saving on busbar cost is of order 30%. The DOE analysis reportedly shows that without HTSC, Tokomak busbar costs (considered in detail for at least designs) would be on the same order as those computed for fission reactors (LWR, LMFBR) using the same costing models[7]. This is not at all encouraging, since those costs are two orders of magnitude larger than those of saving, through full practical retrofit of existing buildings and equipment with the best commercially available end-use-efficiency technologies, many times the present output of fission reactors[8].

Other applications

There are probably important applications of HTSC materials both in specialized solid-state devices (such as squid magnetic-field detectors) and in high-speed miniaturized electronic devices generally. The implications for computers appear especially favorable. It is not clear, however, that such applications would materially reduce energy use except in computers themselves -- a use currently at or below the ~1% level for virtually all countries (perhaps a few percent for Switzerland).

Applications to educational toys are already on the market. These are fun but do not save energy.

Applications to the production of special materials -- e.g., by magnetocatalysis (which permits unusual chemical reaction kinetics) and by producing a high degree of orientation in metallic materials -- may well exist and be commercially useful[9]. It is not clear what their energy implications might be, but in general the result of lighter, stronger, more specialized materials is to save energy in transportation, not in electrical use.

Conclusions

The overall net effect of HTSC would almost certainly be to reduce the use of electricity, not to increase it. This reduction could in principle, with cost no object, be significant (on the order of perhaps 20-50 GW in the U.S., for example, worth several G$/GW in avoided cost to the utility system). However, it is very clear that enormously larger amounts of electricity can be cheaply saved today by retrofitting commercially available technologies (chiefly in lights, motors, appliances, and building components) which have nothing to do with HTSC. The roughly quadrupled efficiency potential already identified with the best commercially available end-use-efficiency technologies[10] would leave little for HTSC to save.

The "negawatt revolution" is as new as HTSC: most of the best electricity-saving devices on the market today weren't available a year ago. It is also much more important to energy policy than HTSC. Yet, in contrast to the media hype devoted to HTSC[11], conventional end-use efficiency has received almost no attention.

In summary, therefore, successful HTSC would be important for big, fast electronics, for specialized solid-state devices, and for big-magnet uses. These should all have only very slight effects, probably negative, on electric use (electronics probably uses <2% of present total U.S. electricity). HTSC bulk power transmission and HTSC-storage cars do not look very attractive. Motor savings will be worthwhile but a tenth as big as non-HTSC drivesystem savings. Thus the major implications of HTSC will probably be in computing, not in energy policy.

In energy efficiency, HTSC offers modest, incremental improvements which may be worth pursuing and which could prove quite profitable in those particular instances where a HTSC device is competitive with a copper or aluminium device.

But HTSC's potential energy savings should not divert attention from the much larger, cheaper, and easier savings available now from techniques already proven and available.

(1) The author is indebted to Oliver Sparrow of Shell for pointing out that since superconductors can be good conductors of heat as well as of electricity, they might in certain circumstances have important applications in "super-heat-pipes" and other heat-transfer devices.

(2) A.B. & L.H. Lovins, Brittle Power: Energy Strategy for National Security, Andover, Massachusetts: Brick House, 1982, summarized in The Atlantic Monthly, November 1983; ca. 1200 references.

(3) See, for example, any recent issues of Microwave News, a bimonthly technical newsletter edited by Dr Louis Slesin, PO Box 1799, Grand Central Station, New York NY 10163, 212/517-2800.

(4) See A.B. Lovins et al., The State of the Art: Drivepower, Rocky Mountain Institute, in preparation, January 1989 (a proprietary report of the I Institute's Competitek update service).

(5) Approximately eight manufacturers have already demonstrated internal-combustion-engine 4-passenger prototype cars with efficiencies of at least 29 km/l, with some achieving up to 51 km/l. At least two such prototypes with efficiencies upwards of 31 km/l have a reported marginal production cost of approximately zero.

(6) K.S. Demirchian, "Superconducting Systems of Advanced Sources of Electrical Energy in the USSR," unpublished manuscript, 1987, USSR Academy of Sciences, Moscow, 21 pp.

(7) Of course, those costing models have proven wildly inaccurate for fission, but perhaps their inaccuracies might be equal for fusion. More likely, the inaccuracies might not be simply extrapolable to fusion; the models certainly do not handle satisfactorily the values or the evolution over time of the capital-cost divergence between coal and nuclear stations.

(8) For example, recent analyses at Rocky Mountain Institute show an approximate potential to save about 50% of U.S. electricity at zero net cost, or 75% at an average cost below 1 US cent per kW-h (probably nearer one-half cent per kW-h), while providing unchanged or improved energy services.

(9) Tom Schneider is currently coordinating a $1 million Electric Power Research Institute research program on such potential applications.

(10) Joergen Noergaard at the Technical University of Denmark has recently identified in Danish buildings' electrical uses (excluding lighting, whose savings are larger and cheaper) the same potential noted above for all US end-uses -- quadrupled efficiency at ~0.6 US cent per kW-h average cost.

(11) This includes extraordinary assertions that HTSC will save most of our current electric (or, even, of our total energy) usage. Such claims may perhaps arise from a psychological need, after Bhopal, Challenger, and Chernobyl, to reassert the mythic omnipotence of high technology.

HTSC - an overview of present activities and their impact in India

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Abstract

A general overview of all possible applications of these high temperature superconductors is given. Technical limitations involved in such large scale applications have been enumerated briefly in a simplified manner.

Once the initial excitement of the discovery of HTSCs is over and the dust settles down, it would not be difficult to see that this discovery is perhaps not as revolutionary as the discovery of the phenomenon of superconductivity. Yet while Heike Kamerlingh Onnes discovered superconductivity in 1911, even in 1988 it is only being used effectively in magnets for fusion experiments and accelerators. I point this out, not with an intention of underplaying the importance of this discovery, but to put into perspective the fact that what might appear like one easy step in converting an idea into a technology really demands several new innovations. There were several steps in going from discovery of nuclear fission to commercial nuclear power. The discovery of HTSC has just indicated that superconductivity is indeed possible at higher temperatures in systems which have not yet been discovered and understood. the oxide system is one such - may be there are many others in which the parameters might turn out to be more suitable for applications. It can therefore, be rightly said that this discovery has opened up a new field of activity with great promise.

There are many examples that one can quote to show that converting an idea into a technology which is economically useful to the society takes several decades. The main factors which determine the speed with which this can occur are the following. A society has to have the culture which drives it to industrialization by quick utilization of good scientific ideas. Very often applications in Defence have rightly or wrongly provided the motivation. This not only measures the economic shrewdness with which the society is governed but also the trades and crafts which it has managed to develop. In other words this could be called the measure of stress that is laid on applied research vis-a-vis basic research. The intention is not to start a debate on which of these is more important but to determine the relative balance between the two. The other factor which determines the speed of this transformation of ideas into technologies is the technical base which is available in a country. As money begets money so also technology begets technology. It should, therefore, not be surprising that while HTSC materials were discovered and made almost simultaneously in many countries, the utilization of these materials in the industrial sector will have a big spread. It is in this context that one has to inspect the future impact of HTSC in India.

The initial excitement at the discovery of this material was because of its much higher critical temperature, at which the electrical resistance falls to zero. While the known metallic superconductors could reach zero resistance at about 20 K, the new material could achieve the same at as high as 90 K. This meant change in the cryogenic from liquid helium (boiling point 4.2 K) to liquid nitrogen (boiling point 77 K) which is quite easily available, and at much less cost. However, there are two other properties of the superconducting materials which are also crucial for its performance. In addition to the critical temperature (Tc) one has also to consider the density of the current (Jc) which can flow through this material and the strength of the magnetic field (Hc) that the material can tolerate in its superconducting state. While the critical temperature and the critical field are the basic properties of the material, the critical current density can be influenced by the processing techniques. The initial euphoria was because of high Tc. The subsequent characterization in terms of Jc and Hc, as well as some other properties has sobered the response of applied scientists to this material.

Table 1

Energy	:	Nuclear Fusion
		Magnetohydrodynamics (MHD)
		AC and DC generators
		Energy Storage
		Power Cables

Table 1 Contd ...

Industry	:	DC Motors
		Magnetic Separation
Transportation	:	Maglev Vehicle
		Propulsion
Medicine	:	Magnetic Resonance Imaging
		SQUID/Magnetocardiography
High Energy Physics	:	Accelerators (synchrotrons & cyclotrons
		Particle Detectors
		Wigglers
Research and Development	:	High Magnetic field
		Sensors (temp., magnetic field, field gradient, current, emf, phonon)
Electronics	:	Josephson Junction
		Magnetic Shields
		Signal Processors (amplifiers, mixers, delay lines, digital devices)
		Inter Connections on ICs (Inter chip and on-Board inter connects)
		Strip Lines for Signal Propagation
		Infra Red Detectors

Table 1 gives the major applications that super-conducting materials can be made use of. Since considerable literature has already been generated on the applications of HTSC materials for revolutionizing the industrial capabilities in a variety of fields, I would not reiterate these uses. I would rather mention some of the technical limitations of this new material. This would help in understanding the large task which faces scientists and engineers who have to use this material for specific applications.

1. While conventional shapes like rings and discs are relatively easy to make, HTSC materials like all ceramics, are brittle and therefore difficult to fabricate into tapes and wires. The present HTSC materials are also found to be very sensitive to oxygen, water and carbondioxide in the atmosphere and the rate of environmental degradation is quite high. While several methods for encapsulation can be developed for production of this material, this remains a basic handicap.

2. HTSCs are anisotropic materials with their ability to conduct current varying to a large extent with the crystal axes. Hence it is feared that the question of fabricating conductors with this material would have to contend with factors that determine grain orientation.

3. Earlier experience has shown that the properties of a superconductor deteriorate as it approaches its critical temperature. Therefore, it was recommended that LTSCs should be operated at about half their critical temperature. This would seem to imply that if a material was to be used in an industrial application at liquid nitrogen temperature, its critical temperature should be in the neighbourhood of 150 K. This, as we know, is substantially above the materials known today.

4. It has to compete with materials like NbTi which at liquid helium temperature can generate fields upto 9 Tesla which is nearly 5 times that of iron magnets. for comparison it may be noted that one Tesla is equal to about 20,000 times the earth's magnetic field. The other superconducting material for which relatively difficult fabrication problems are now solved is Nb^3 Sn. This can support fields as high as 15 to 16 Tesla. The upper critical field of the HTSC is being estimated as 250 to 350 Tesla at absolute zero. However, the critical fields at liquid nitrogen temperature are likely to be much smaller. The resistance is reported to reappear at less than 10 Tesla.

5. However, the most important limitation appears to be the critical current density. In thin films critical current density upto 10^5 Amps/cm^2 have been reported.

The highest value in bulk samples at liquid nitrogen has been reported to be about 10^3 Amp/Cm^2 at 1 Tesla. This could be a very big limitation for us in motors, generators, magnets and power lines where current densities upto 10^5 Amps/cm^2 are needed.

An even larger question arises regarding utilization of HTSCs in relation to its economic impact on specific applications. Take, for instance, the magnetically levitated trains. The idea has been mooted years back and the arrival of HTSC was immediately connected with the success of this method of transport. However a detailed look reveals that the economics of a venture of this kind hardly depends on the cost of the cryogenic to be used. The larger issues which determine the cost of such projects in addition to technological limitations, are procuring the ground for the tracks, building bridges, laying tracks with precise geometry, safety systems, etc.

Similarly, one of the largest experiments using superconductivity being talked about is the Superconducting Super Collider (SSC), an accelerator which is expected to cost more than 5 billion dollars. From the preliminary design, it is expected that thousands of high field magnets may be needed for this. Obviously, this could be an important area for HTSC magnets. But the fact is that only 5% of this total cost of the accelerator is expected to be spent on magnets. The figure of 250 million dollars is rather small when compared with the total expenditure. On the other hand, even if HTSCs are used it might well turn out that liquid helium would still be the cryogenic needed because of the high vacuum requirements of this system.

Transmission lines are another important area in which the impact of HTSC technology was expected to be large. For obtaining some quantitative idea, the total consumption of electricity in U.S.A. in 1985, was worth $175 billion. It was estimated that the transmission loss amounted to about 5%, making this loss worth about $8.75 billion. By itself this might appear a big figure but when considered alongwith the fact that the installation cost may work out in hundreds of billion dollars, the economic feasibility of this idea appears rather limited. Obviously if HTSC transmission lines were to be used they would have to be underground which are estimated to be 10 to 30 times more expensive than overhead transmission lines. However, this may become competitive when fresh lines are required.

The general opinion of the experts today is that HTSC may give a decisive economic advantage in the kind of small magnets used in NMR device for imaging. This is based on the fact that smaller magnets have higher cost component from the cryogenics.. Similarly, with the available information, there seem to be some very feasible and important uses in micro applications like Josephson Junctions and Squids. But it is difficult to see any significant economic impact of such developments. Keeping in mind these considerations, it seems inevitable that while India could be in the forefront of basic research on HTSCs, its velocity of achievements in applications could well be slower than those of advanced countries. This is a reality we must face in light of the infrastructure available within the country and a limited number of institutions with tradition in applied research. As far as making magnets are concerned it could proceed faster with groups that were working with LTSC. But in India there are very few such groups. But there is no room for pessimism. In fact with the kind of attention and support that the Government of India is already giving to this field, HTSC could very well provide the test ground for India to make an effort and learn the tricks needed to convert ideas into technologies. After all there have been successful experiments with advanced technologies like nuclear and space where the country has succeeded in a large measure.

Oxygen in high-TC superconductors - effects, problems and solutions

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Abstract

The role of oxygen content in the material properties of superconducting oxide ceramics is reviewed with special reference to yttrium barium cuprate, $YBa_2Cu_3O_{7-\delta}$ and its derivatives. The twin problems of slow oxygen loading in dense material and the occurrence of microcracking due to non-uniform and highly anisotropic thermal expansion are addressed and a variety of processing routes designed to minimise these effects are discussed. These include cation substitution to enhance diffusion coefficients, electrochemical insertion of oxygen and processing below the orthorhombic to tetragonal transition temperature.

Introduction

Electronic effects in oxide ceramics have been studied and applied for many years, and are the basis of a rapidly expanding industry (1,2). Though traditionally thought of as insulators, ceramics span the full range of electronic materials including insulators, fast-ion or superionic conductors, semiconductors, metallic conductors and, of course, now superconductors as exemplified by $La_{2-x}Sr_xCuO_4$ (3), $YBa_2Cu_3O_{7-\delta}$ (4) and the recently discovered $(Bi,Tl)_2Sr_2Ca_nCu_{n+1}O_{2n+6}$ (5,6). The latter three materials and a large number of derivatives are referred to as high-Tc superconductors with transition temperatures, Tc of the order of 40 K, 90 K and 125 K respectively. They are, however, not the first oxide ceramic superconductors to be discovered. That status is reserved for $LiTi_2O_4$ (7) which was found in 1973 followed two years later by $BaPb_{1-x}Bi_xO_{3-\delta}$ (8) both of which have Tc ~ 13 K, insufficiently high at the time to have initiated widespread interest. In most of these oxide ceramics the oxygen content or stoichiometry is variable to a greater or lesser extent and this variability can have a profound effect on the electronic structure of the material determining ultimately whether it is an insulator, semiconductor, metal or superconductor. The best example of these effects happens to be found in $YBa_2Cu_3O_{7-\delta}$ (YBCO) which occupies the six different categories listed in Table 1 depending on the value of d. Similar, though less marked behaviour may also be seen in $La_2CuO_{4-\delta}$, $La_{2-x}Sr_xCuO_{4-\delta}$ and $BaPb_{1-x}B_{ix}O_{3-\delta}$. Moreover, measurements of diffusion coefficients for oxygen in YBCO from ultrasonic mechanical damping shows a diverging diffusivity of oxygen in the lattice starting at $\delta = 0.25$ (9) so that the material increasingly behaves as a fastion or superionic conductor thus offering, in addition, a variety of electrochemical applications or processing routes.

Table 1. The dependence of the different electronic states of $YBa_2Cu_3O_{7-\delta}$ on oxygen stoichiometry, δ .

State	δ	**Crystal Axes**
Semiconductor	0.8 to 1.0	
Metal	0 to 0.8	
Non-superconductor	0.55 to 1.0	$a = b < c/3$
Superconductor Tc ~60 K	0.2 to 0.55	$a < b < c/3$
Superconductor Tc ~90 K	0 to 0.2	$a < b = c/3$
Incipient fastion conductor	0.25 to 1.0	

The following work will focus on these effects in YBCO and their implications for a wide variety of material properties. The variable stoichiometry offers a useful means of tailoring properties, but also introduces a number of problems such as cracking and prohibitively slow oxygen loading in the dense ceramic. This will be discussed together with a number of possible solutions and applications. While a great deal of research has been directed at this material in the last 12 months, one must warn that the subject is still in its infancy, many of the results are tentative and conclusions should be seen as guidelines only. Moreover, the development of new materials possibly heralded by the bismuth and thallium cuprates may circumvent some of the problems alluded to. We therefore proceed recognising on the one hand, that the field is rapidly evolving and on the other that some of the results will be generally applicable to the wider class of oxide superconductors including any new entries. It should be remembered that oxygen stoichiometry is only one measure of superconducting quality and that other, in some cases more difficult, criteria have to be satisfied. The most demanding of these relates to the intergranular structure as it effects critical currents.

Oxygen content and superconductivity

Fully oxygen loaded YBCO is unstable at the high temperatures of reaction and at sintering temperature of at 890 to 950°C. This is readily demonstrated by the inability to prepare YBCO in ambient oxygen at pressures beyond several times atmospheric pressure. It is fortunate that the rather narrow stability range spans oxygen partial pressures including that of air and pure oxygen. Reacted in air at 950°C the material is rather oxygen deficient with $\delta \sim 0.73$ but this deficiency is temperature dependent and if the material is slowly cooled it will progressively load up with oxygen until ultimately $\delta \sim 0$ at about 400°C (10). This is the optimum state for high temperature superconductivity as we shall see. This oxygen loading is an equilibrium process and at any given temperature and oxygen partial pressure, if enough time is allowed for inward or outward diffusion of oxygen, the oxygen deficiency, δ will equilibrate at some reproducible value. At this point let us note that the diffusion rate is a key element in this and if it were too slow the crucial oxygen loading might never be achievable. In dense material this turns out to be a major problem, which will be discussed in detail later.

Fig. 1 shows equilibrium values of the oxygen deficiency, as a function of temperature for a range of different oxygen partial pressures (10). The material is fully loaded at about 400°C and no further loading occurs at lower temperatures. This plot illustrates the benefit of 'soaking' the sample at ~450°C after a slow cool so as to ensure well equilibrated fully loaded material. We will see that mere loading is not sufficient and that the oxygen must also become fully ordered within the material for optimised results. The effect of oxygen loading on superconductivity may be demonstrated by annealing a sample at a fixed temperature in air then rapidly quenching the sample into liquid nitrogen so as to freeze in the equilibrated oxygen content (11). Diffusion rates at room temperature are sufficiently low, that the frozen value of δ does not alter before Tc measurements can be completed. On the other hand loading and diffusion at the anneal temperatures is sufficiently fast that δ changes appreciably in mere air quenching, hence the need for the rather severe liquid nitrogen quench. There are other yet more reliable methods of obtaining a uniform prescribed value of δ (12). The values of Tc measured for samples with different values of δ are shown in Fig. 2 (12). One sees a marked dependence with two plateaux: one at 90 K for $\delta < 0.2$ and another at 60 K for $0.2 < \delta < 0.5$ followed by a sudden loss of superconducting behaviour at $\delta = 0.55$ and beyond. More recent work (13) shows the step from 90 K to 60 K superconductivity to be very sharply defined. The significance of this two-step behaviour is not fully understood, but the need for full oxygen processing in order to achieve 90 K superconductivity is made abundantly clear.

What is, by now, fully understood, are the structural changes which accompany oxygen loading. The structure of YBCO in the fully loaded ($\delta = 0$) state is shown in Fig. 3. This material has two *planes* of copper oxide straddling a sheet of yttrium atoms and copper oxide *chains* sandwiched between two barium oxide planes. It is these copper oxide chains which unload oxygen. Fully loaded, only half of the oxygen sites in the layer of chains are occupied, those referenced in the figure as 01 sites. These form -O-Cu-O-Cu- chains in the b-direction and the remaining 05 sites are vacant. This asymmetry in the plane causes the length of the unit cell in the b-direction, the b-axis, to be slightly larger than the a-axis and the structure is therefore orthorhombic. With rising temperature, two effects take place (14). Some oxygens progressively *disorder* from the chain 01 sites onto the 05 sites, and others, assisted by the disordering, diffuse through the plane and *unload* at the surface. The disordering becomes increasingly rapid until suddenly the 01 and 05 sites are equally populated at which temperature the layer becomes symmetric, and the a-axis equals the b-axis. The material is now tetragonal and remains so for all higher temperatures. Only the orthorhombic material exhibits superconductivity and thus the orthorhombic to tetragonal (O-T) transition temperature, for which $\delta \sim 0.55$, marks the limit for structures which will superconduct. The resulting dependence of the a-, b- and c-axes on temperature (15) is shown in Fig. 4. The purpose of slow cooling in air or oxygen is to reverse these processes allowing both oxygen loading and oxygen ordering to occur. Theoretical calculations (14) of the occupancies X_1 and X_5 of the 01 and 05 sites are shown in Fig. 5 and are compared with experimental measurements from neutron diffraction. The sample is fully ordered when $X_5 = 0$ and $X_1 = 1$. The oxygen loading curve is given by the dash=dot curve and while the *loading* is complete at ~400°C full *ordering* is not achieved until below ~200°C.

One further link between structure and superconductivity should be noted. The 90 K superconductor happens to have a c-axis which is three times as long as the b-axis. With the 60 K superconductor, i.e., for $\delta > 0.2$, this no longer holds.

These structural relationships between the a-, b-and c-axes are summarised both in Table 1 and in Fig. 4 and of course, they provide an independent means of determining, by for example x-ray diffraction, as to whether a material will be a superconductor and, if so, what kind. If during manufacture the material has been cooled too rapidly, or with insufficient ambient oxygen, then any of the higher temperature states may be frozen in with a resultant greater oxygen deficiency. It is of course, a great benefit that Tc remains unchanged between $\delta = 0$ and $\delta = 0.2$ so that small oxygen deficiency can be accommodated with no drop in transition temperature. A more important question though, is whether the critical current falls off rapidly with small levels of oxygen deficiency. At the moment, insufficient information is available to answer this question, but one would expect that as the critical current in the present generation of high-Tc materials is determined by the quality of the boundaries between grains and as grain boundaries are the first regions to load up in oxygen, they will be unaffected by small levels of deficiency within the grains themselves. The bismuth and thallium superconductors have been reported to be less prone to oxygen loading effects. This is not the case (6). Indeed the question of oxygen stoichiometry in these materials is rather more complicated than in YBCO. Tc for the phase $Bi_2Sr_2Ca_1Cu_2O_{8-\delta}$ can be increased from 80 K to 91 K by rapid quenching from 960°C. This freezes in an apparently beneficial oxygen-deficient state, which on lower temperature annealing is redressed with a resultant return to 80 K superconductivity. On the other hand, the higher-Tc phase $Bi_2Sr_2Ca_2Cu_3O_{10-\delta}$ (Tc = 105 K) and its thallium counterpart (Tc = 125 K) are promoted by lower temperature annealing in air or oxygen (5,6). The precise structural and electronic effects of oxygen stoichiometry awaits further clarification.

Oxygen content and material properties

It is difficult to locate a single material property of YBCO which is not affected by oxygen stoichiometry. However, the details of many of these physical properties are beyond the scope of the present work, and we shall consider mainly those that have some bearing on applied superconductivity. Focus will be drawn to factors which cause problems of microcracking and difficulties in oxygen loading or which offer useful steps in processing of the materials.

Thermal expansion

Fig. 6 shows the temperature dependence of a number of material properties of YBCO above room temperature (16), including the volume thermal expansion coefficient, α_v and the oxygen stoichiometry $(7-\delta)$. α_v is about $11.5 \times 10^{-6} K^{-1}$ at room temperature, rather typical of oxide ceramics, but starting at about 400°C the expansion coefficient more than doubles to $28 \times 10^{-6} K^{-1}$ before falling back to a normal value near the O-T transition. This expansion anomaly can be seen to commence as oxygen starts to unload and arises from the additional repulsion between the lone copper atoms and the barium atoms above and below. Such large changes in expansion coefficient are bound to present problems arising from the additional stresses on the ceramic. Worse still is the fact, shown in Fig. 4, that the expansion is different for the different crystal axes, and indeed involves a contraction in the b-direction. This large anisotropy coupled with problems of non-uniform loading of oxygen, often causes extensive microcracking in the material as it cools down. Consider that a grain loads oxygen from the outside and therefore contracts in the outer shell more than the inner core. This places the outer shell under *tension* which will promote cracking. The problem does not arise during heating, e.g., prior to sintering, as the outer shell is then subjected to *compression*. Evidently the immediate solution to this problem is to cool very slowly so as to ensure uniform loading of oxygen, but in dense samples we shall see that the oxygen diffusion coefficient is too low to ensure uniformity and it is in the most dense samples that cracking is most prevalent.

Oxygen diffusion

Also shown in Fig. 6 is the mechanical damping of a sample subjected to a 40,000 cycle per second vibration. A marked peak in the damping occurs at 520°C which can be attributed to the 01 oxygens being driven back and forth into the 05 sites by the cyclic stress. From this the oxygen diffusion coefficient may be calculated to have the unfortunately low value of $D \sim 8 \times 10^{-12}$ cm^2/sec (9). To see the implications of this, consider a flat plate of 100% dense YBCO just 1 mm thick. It will take 600 days for the oxygen to diffuse into the centre. The reason why in practice one can load YBCO with oxygen is that, prepared by normal ceramic routes, this material is only 75 to 85% dense, and it consists of grains of the order of 5 um in diameter. Oxygen can move through the pores and has only to diffuse 2 or 3 um into the grains taking about 103 seconds to do so. The greater the density and the better sintered the ceramic the more difficult it is to achieve stoichiometry for superconductivity and the more prevalent is the microcracking. Microcracking of course, not only limits strength and fracture toughness, but it presents a mosaic of breaks in the superconducting pathway. Supercurrents may tunnel though some microcracks but the critical current is greatly limited.

Elastic stiffness moduli

The final quantity described in Fig. 6 is the elastic Young's modulus for YBCO at elevated temperatures. Knowledge of the elastic moduli and their temperature dependence is important for a variety of fundamental and applied questions including those of engineering design, fracture toughness, structural instabilities and the thermodynamics of the superconducting transition. Full characterisation of the elastic properties requires the determination of the nine independent moduli for a single crystal with orthorhombic symmetry. This has not yet been done because the largest single crystals are still too small to carry out the measurements. For an untextured or unoriented polycrystalline ceramic the number of independent moduli reduce to two: the rigidity or shear modulus, G; and the bulk modulus, B. Other derived moduli include the Young's modulus $E = 9GB/(3B+G)$ and the Poisson's ratio $\nu = (3B-2G)/2(3B+G)$. E and G have been measured from the change in resonant frequency of long sintered rods of YBCO vibrating longitudinally ($\ell = 45$ mm) and torsionally ($\ell = 36$ mm) respectively at about 40 kHz. The various room temperature moduli obtained with this technique and corrected for porosity are listed in Table 2. These agree well with measurements using other methods.

Table 2. Elastic moduli and Poisson's ratio for YBCO at room temperature.

Young's modulus, E,	104 GPa
rigidity modulus, G	39 GPa
bulk modulus (adiabatic), Bs	115 GPa
longitudinal modulus, C_{11}	167 GPa
Poisson's ratio, ν	0.35

The temperature dependence of the modulus E shown in Fig. 6 displays a prominent soft mode cusp at the O-T transition arising from softening due to the orthorhombic strain fluctuations which occur on approaching the transition. There has been some controversy regarding whether the O-T transition is first or second order. The behaviour shown in Fig. 6 is characteristic of a fluctuation-driven second-order phase transition. The effect is even more marked in the shear modulus which softens by nearly 50%. By changing the ambient oxygen partial pressure the cusp is displaced to lower or higher temperatures and this provides a very precise means for accurately locating the O-T transition (16). Of greater interest is the possibility of *superplastic* behaviour associated with the soft mode cusp (17). Superplasticity refers to the occurrence of large (up to several hundred percent) uniform strains under deformation without fracture. It may occur in certain fine grained mixed phase bodies, and sometimes in the vicinity of fluctuation driven structural phase transitions, e.g., zirconia near the martensitic tetragonal to monoclinic transition. Extrusion or drawing at the O-T transition has been proposed as a novel processing method to assist in preparing long oriented filaments (17), however, preliminary measurements on rods under three-point bending failed to demonstrate any superplastic behaviour near the O-T transition. These measurements were carried out in air for which T_{OT} ~640°C. This temperature is probably too low for plastic flow of any kind, and it may be necessary to work at higher temperatures increasing the oxygen partial pressure to raise T_{OT} to the operating temperature.

Microstructure

The microstructure of the ceramic is dominated by its granular structure, with random orientation of grains, pores and segregation of impurity phases at the grain boundaries. All of these introduce serious limitations on critical current. Apart from pervasive carbonate in porous samples, the principal impurities at the boundaries for stoichiometric material are CuO and $BaCuO_2$ as these form the flux from which the YBCO material tends to grow (18). Stoichiometry is balanced by the incorporation within the YBCO of regions of the green phase Y_2BaCuO_5 [211] and because this tends to be engulfed, the latter phase is not so harmful. One approach to minimising these effects is to eliminate the flux by reacting the sintering below the solidus line thus employing a wholly solid state reaction. This inevitably leads to very slow inhomogenous reaction with high porosity unless assisted by the use of very fine highly reactive particles. This is a legitimate approach, but to date, little has been achieved along these lines.

At the other extreme much is now being accomplished by methods of melt processing (19) where either time spent in the melt phase is kept sufficiently short to minimise phase segregation, or high oxygen overpressures (500 psi) are used to prevent peritectic decomposition. In this way close to 100% density can be achieved with extensive elongation and alignment of YBCO crystals in vicinal contact. The inevitable small percentage of entrapped impurity phases does not seem to be a problem, the essential feature being that the impurities are not distributed over the entire grain boundary surface. In this way critical currents of 1.7 x 10^4 A/cm^2 can now be achieved at 77 K in zero field - close to that for single crystals.

So much for extrinsic microstructure. In addition, YBCO has an intrinsic microstructure in the twin domains arising from the O-T transition (20,21). We have referred to the highly anisotropic thermal contractions associated with cooling through this transition. Excessive shear strains are typically averted in this kind of transition by the spontaneous formation of consecutive structural bands known as twins, where the a- and b-axes are interchanged. This is shown in Fig. 7 and the structure of the [001] basal CuO plane with a single twin plane (TP) is illustrated in Fig. 8. Other defects are shown in the figure with some oxygens disordered from 01 sites onto 05 sites. The planar twin boundary can be seen to naturally lie on the [110] planes and from nearest neighbour oxygen interactions we estimate the twin plane energy to be 2.5 x 10^{-2} J m^{-2} (14) very typical of the magnitude of such in a variety of materials. In contrast a grain boundary energy may be 20 times larger so these low energy twin boundaries are typically difficult to anneal out. The effect of twin planes on superconductivity is not as yet clear and various opposing views have their proponents:

(a) One view is that twin boundaries may be intrinsically semiconducting and are traversed only by *tunnelling* supercurrents. This would tend to promote superconducting loops confined to a twin domain resulting in the so-called 'superconducting glassy state" providing intrinsic, rather than extrinsic, limitations to critical currents (22). This view would see the elimination of twins as an important goal in materials processing.

(b) Others argue that twins promote higher Tc's either by a proximity effect (23) or by the induced changes in the phonon spectrum (24). It is also widely believed that twins may play an important role in pinning flux and could be tailored to enhance critical current and upper critical magnetic field. This kind of microstructural texturing is widely used in conventional A15 superconductors to improve critical parameters (25). It must be emphasised, however, that the gains to be had are less than a factor of ten whereas the granular and impurity phase microstructure is responsible for deficits in critical parameters by a factor of one thousand or more.

(c) A third view which has emerged with the appearance of the bismuth and thallium superconductors is that twins really have little effect on superconductivity. These materials have done much to dispel a number of "myths" in high-Tc superconductivity: the copper oxide *planes*, not the *chains*, provide the superconducting pathway as there are no chains in these compounds; and, concerning the present point, the structural common denominator in all previously known oxide superconductors was their orthorhombic structure - however, some of the thallium superconductors are tetragonal and consequently are completely lacking in twin features (5).

Many other material properties which are markedly dependent on oxygen stoichiometry could be enumerated, but these have rather less bearing on aspects of applied superconductivity. Brief mention should be made of just two more properties which may provide a useful quick means of assessing the oxygen deficiency δ in $YBa_2Cu_3O_{7-\delta}$ and oxide superconductors in general. Firstly, a number of infrared absorbtion lines show continuous changes with δ probably the most useful being the 504 cm-1 line ($\delta = 0$) which falls uniformly to ~475 cm-1 as δ increases to $\delta = 1$ (26). Secondly, the electrical resistivity exhibits a simple dependence of δ which is more or less independent of temperature (27). Either of these properties, though more feasibly the second, could therefore be used with appropriate calibration to assess the oxygen stoichiometry following or even during processing.

In summary two major related problems occurring with $YBa_2Cu_3O_{7-\delta}$ have been highlighted, namely

(a) oxygen loading of *dense* material by diffusion occurs too slowly for practical purposes if the material dimension exceeds about 0.5 mm, and

(b) the non-uniform and anisotropic thermal expansion arising from oxygen loading in dense material causes microcracking with serious effects on critical currents. Some of the methods available for circumventing these problems will be briefly discussed. It is too early to assess which route is the most appropriate, but this summary will indicate the areas where further work could be most fruitful.

Possible solutions to the diffusion and microcracking problems

Small scale processing

Possibly the most direct means for improving the kinetics of oxygen unloading is to limit bulk material dimensions or maintain porosity. According to the simple laws of diffusion, diffusion time is proportional to the square of the diffusion distance. Consequently reduction in the oxygen diffusion path length very quickly decreases the diffusion time. Filiaments less than 0.1 mm diameter or thin films should present no difficulties in oxygen loading. There are other mechanical and electrical engineering reasons for adopting a multifiliamentary configuration and this is widely used for the conventional A15 superconductors (25). There appears therefore to be no obvious incompatibility in the basic thermal, mechanical and electrical requirements for the multifiliamentary route. One has only to choose a suitable matrix material which should provide:

- mechanical support to the brittle superconductor;
- a low resistance shunt pathway should Tc be exceeded;
- is chemically inert with respect to the superconductor; and
- is suitably porous to oxygen.

Fortunately, silver admirably satisfies each of these requirements as oxygen can diffuse through the metal at elevated temperatures (18). Oxides of silver break down at elevated temperatures to the extent that AgO powder may be used as a heterogeneous oxidant mixed in with the superconducting powder prior to sintering. Moreover the use of AgO assists in the preparation of the 105 K superconductor $Bi_2Ca_2Sr_2Cu_3O_{10-\delta}$ (6).

Alkali substitution

Preliminary experiments indicate that the substitution of potassium for barium in $YBa_2Cu_3O_{7-\delta}$ greatly enhances oxygen diffusion rate without substantially compromising superconducting properties (28). Potassium has the same ionic radius as barium and though of different valency will directly substitute for barium up to at least a 10% level. The optimum level seems to be at about 5% where Tc may have dropped ~2 K only. The effects are usefully disproportionate to the quantity substituted, eg 5% substitution of K for Ba results in a 50% reduction in oxygen in the basal plane. Consequently not only is the oxygen diffusion coefficient increased but the amount of oxygen loading required is halved. The effect of substitution of the other alkalis Li, Na and Rb has yet to be determined.

Electrochemical insertion

The diffusion coefficients quoted above are, in fact, "self diffusion" coefficients, ie, they describe the random diffusion of isolated oxygen atoms. The quantity of real interest in an oxygen loading problem is the "chemical diffusion" coefficient which describes the diffusion of an oxygen under some driving force and of course, the diffusion is more rapid. This force may arise from a concentration gradient as in normal oxygen loading or it may be induced by the application of an electric field in electrochemical loading. YBCO along with many other perovskite related oxides is highly suitable as an electrochemical electrode material (29). It has a high electronic conductivity together with a mobile oxygen ion density and consequently could be used to make a battery or an electrolysis cell. This offers the possibility of electrochemically driving oxygen into YBCO in situ using the material initially as an electrolyte and, as it loads up, ultimately as an electrode. The inverse principle has been applied to determine the thermodynamic stability of YBCO and other related oxides in an electrochemical cell using yttria stabilised zirconia as the electrolyte (30), but as far as the author is aware has not yet been employed to assist in oxygen loading of dense material.

Processing below the O-T *transition*

As the conditions conducive to microcracking occur in the neighbourhood of the O-T transition, benefit could be derived from reacting or sintering at temperatures below this transition. This would also mean that less oxygen need be loaded on cooling. One approach then would be to attempt to displace T_{O-T} to temperatures higher than typical sintering temperatures. By extrapolating graphs of T_{O-T} versus oxygen partial pressure (16) it would seem that this ought to be achievable at about 300 atmospheres oxygen pressure. However, theoretical calculations (14) show that T_{O-T} levels out with increasing pressure at about 772°C. Alkali doping on the barium sites also displaces T_{O-T} upwards (28), but insufficient to achieve anything useful without grossly compromising the superconducting transition temperature. The only useful solution at the moment would seem to be to simultaneously raise T_{O-T} by excess oxygen pressure and drop the sintering temperature by using ultrafine highly reactive particles. Submicron sized precursor or reacted powders will sinter at greatly reduced temperatures, possibly as low as 750°C. Spray pyrolysis can produce fine superconducting powders (31) which, for particle sizes between 10 and 100 nm, are fully oxygen loaded within seconds. It should not be difficult to determine conditions under which such material can be sintered wholly in the orthorhombic state to high density.

These few ideas provide a range of possible solutions to the oxygen loading problem as well as guidelines for further useful research. The ideas focus almost exclusively on a problem which occurs in YBCO. Whether the new classes of ceramic superconductors as they appear will be subject to the same problem remains to be seen. Early work on the new bismuth and thallium compounds confirms that variable oxygen stoichiometry is an important factor in their superconducting properties also and indeed oxygen equilibrium at medium temperatures is achieved rather more slowly than in YBCO. An electron reservoir for "tuning" superconductivity, or more precisely for adjusting the electron Fermi level, seems to be a common feature of all the oxide superconductors and this is achieved by variable oxygen stoichiometry. Looking to the broader scene, it should be noted that many of the ideas presented here are more general than the specific context in which they were presented and could, in principle, be applied to the wider class of oxide superconductors, both known, and yet to be discovered.

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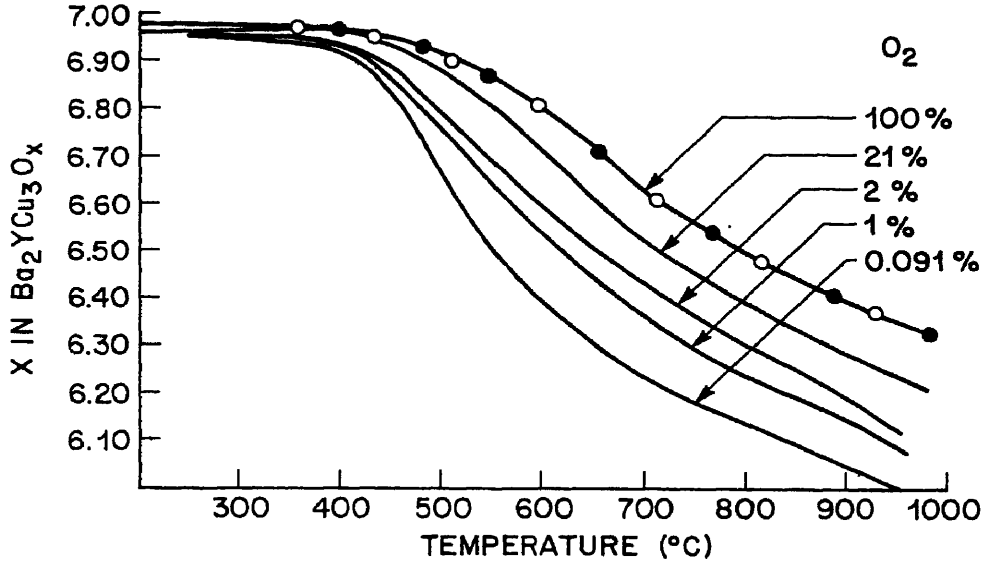

Fig. 1. Temperature dependence of the equilibrium oxygen stoichiometry ($7-\delta$) in $YBa_2Cu_3O_{7-\delta}$ for different fractions of oxygen in the ambient gas at 1 atm pressure.

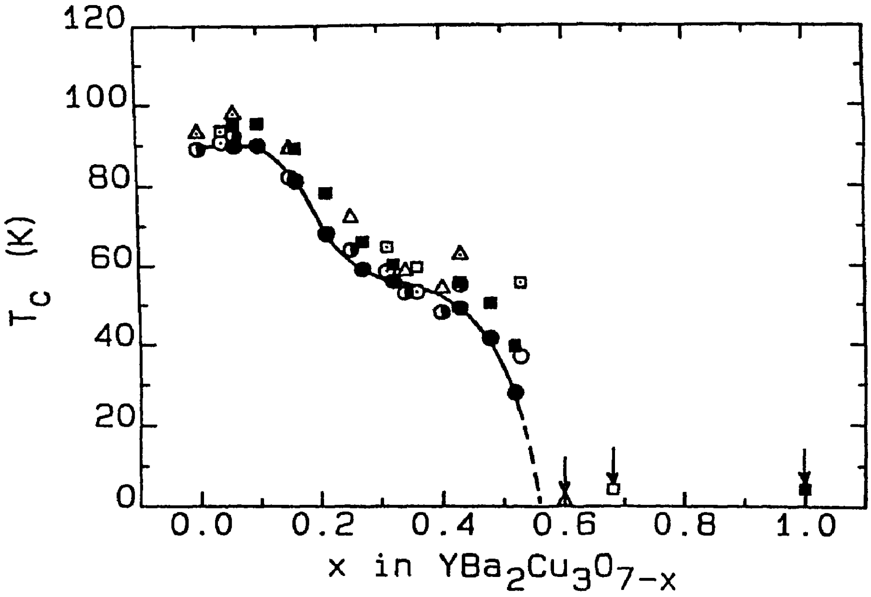

Fig. 2. Values of Tc as a function of oxygen deficiency, δ. Recent measurements (13) show an even sharper change from Tc ~90 K to Tc ~60 K occurring at δ ~0.2

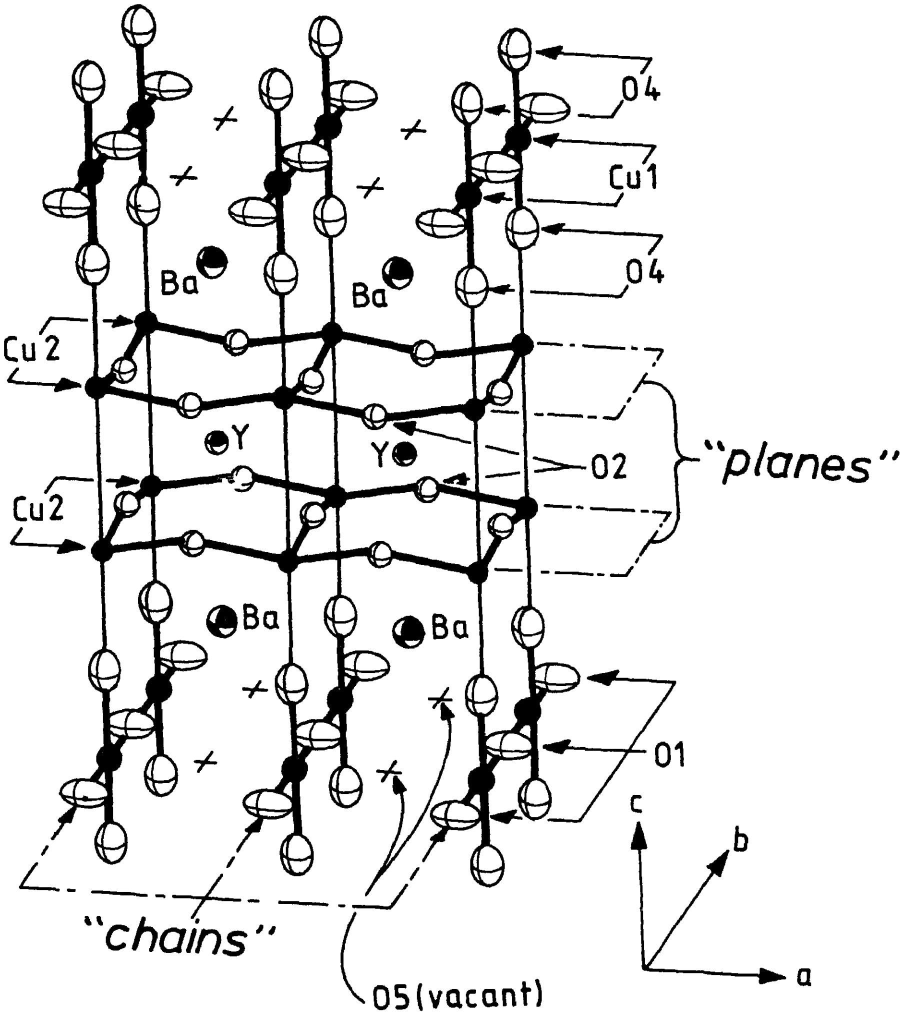

Fig. 3. The structure of fully loaded (δ =0) YBCO showing the characteristic copper oxide planes and chains. As oxygen unloads the 01 sites are progressively depopulated and the 05 sites are increasingly occupied. In the fully unloaded state (δ =1) both 01 and 05 sites are completely vacant.

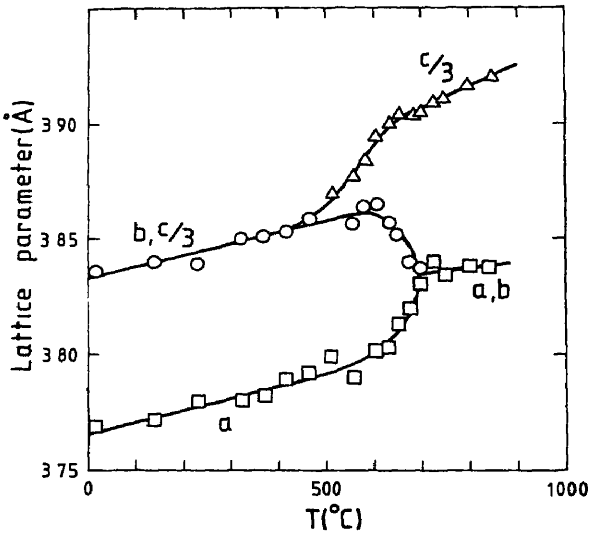

Fig. 4. The temperature dependence of the a-, b- and c-axes of YBCO in air.

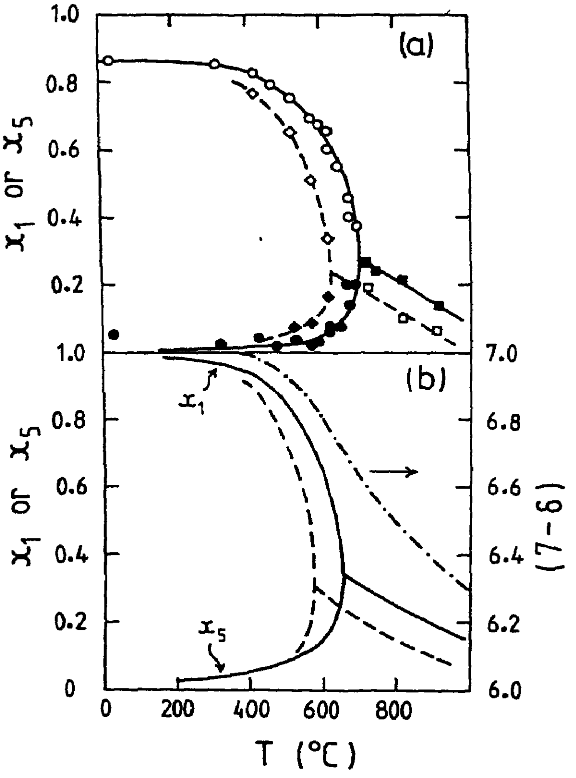

Fig. 5. The temperature dependence of the occupancies X_1 and X_5 of the 01 and 05 oxygen sites (a) from neutron powder diffraction, and (b) from theoretical calculations, ref. (14). The solid and dashed curves are for 1 atm and 0.01 atm oxygen partial pressure, respectively.

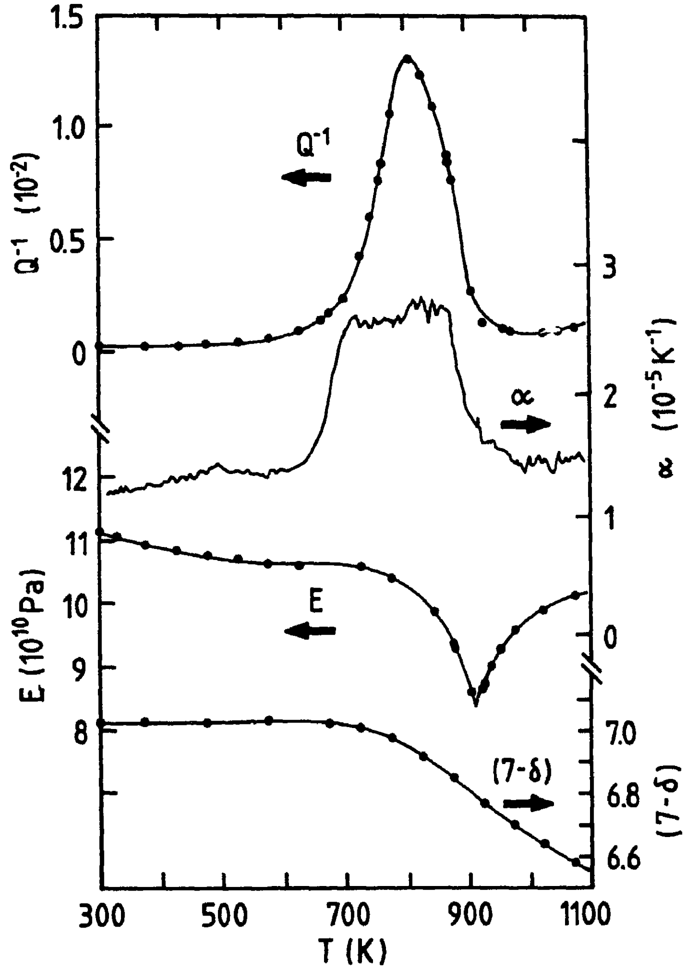

Fig. 6. The equilibrium temperature dependence, for YBCO in air, of the mechanical damping, Q^{-1}, the volume thermal expansion coefficient, α , the Young's modulus E, and the oxygen stoichiometry (7- δ).

Fig. 7. Electron micrograph of YBCO showing twin bands with a characteristic spacing of ~100 nm.

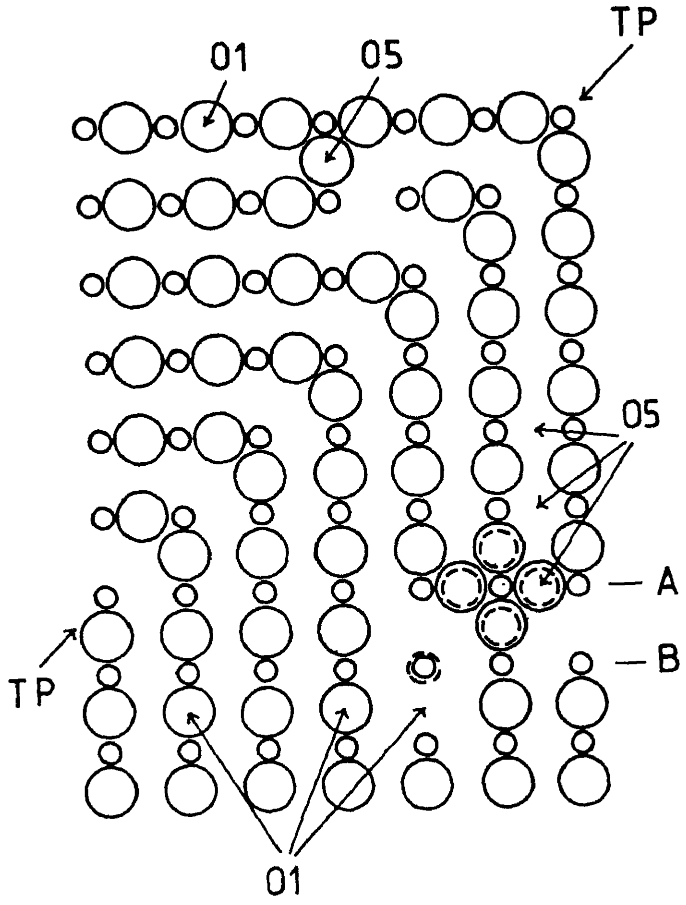

Fig. 8. Schematic diagram of the basal chain layer in YBCO. Large circles denote oxygens and small circles coppers. A twin plane is indicated (TP) where the a- and b-axes of the layer are interchanged. The predominantly filled 01 sites and vacant 05 sites are indicated.

Thermal and electrical conduction (and related effects) in high-temperature superconductors

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Abstract

We review and discuss measurements of the thermal and electrical transport properties of high-temperature superconductors and their interpretation. The thermal conductivity of $YBa_2Cu_3O_7$, which shows a peak below the superconducting transition temperature, is of particular interest, since this peak indicates an unusually strong electron-phonon interaction. This interaction (the source of superconductivity in previously known superconductors) is therefore also likely to make a contribution in the new superconductors. However, radical new mechanisms involving electron-electron interactions have also been suggested as the origin of the new superconductivity. Some evidence in the electrical resistivity in favour of these more exotic interpretations has been proposed, although many features of the transport properties can be interpreted in terms of conventional metallic models. We show how measurements on more disordered samples, that could be made in laboratories lacking the facility to produce single crystals, should help determine how the mechanism of high-temperature superconductivity differs from that previously known. such information is of critical importance in assessing possibilities for the new superconductors.

Introduction

The present quest for yet higher superconducting transition temperatures, following the seminal work of Bednorz and Muller (1), has been handicapped by a lack of understanding of the mechanism producing the spectacular superconductivity discovered by these workers. In spite of an intense international effort to investigate the new materials, there is still much controversy regarding the origin of high-temperature superconductivity. It is possible a completely new mechanism is involved, one not linked to the interaction of electrons with lattice vibrations that is the origin of previously known superconductivity. If this were the case, possibilities for even higher temperature superconductors (in particular room temperature superconductors) look bright, since the superconducting transition temperature T_c would not be limited by the energy of the lattice vibrations. A knowledge of the superconductivity mechanism would help point the way for a more systematic search for materials with higher values of T_c. Thus identification and confirmation of the origin of the superconductivity is of the utmost importance.

There have been tantalizing indications of superconductivity, in the form of a large change in electrical resistivity, at very high temperatures, for example around 230 K, e.g. Huang et al. (2), or even well above room temperature at up to 500 K (3). One of the unsatisfactory features of these observations, however, is that the resistivity in the possible "superconducting" state of the Y-Ba-Cu-O compound of Erbil et al.(3) is still more than a million times larger than that in normal metals. We also find, using the approximate dimensions of the Eu-Ba-Cu-O sample given by Huang et al.(2), that their experimental resolution means that the "zero-baseline" resistivity below 230 K could in fact be as high as 70 $\mu\Omega$ cm, still larger than that of normal metals. Further, the extremely high resistivity (usually decreasing as temperature increases) above the "superconducting transition" resembles semiconducting behaviour. It is therefore conceivable that the observed dramatic decreases in resistivity are due to some kind of semiconductor-metal transition rather than superconductivity. Indications of superconductivity around room temperature through the Josephson effect(3) are perhaps more significant, although indirect.

Our purpose here is to review measurements of the thermal and electrical transport properties of high-temperature superconductors, i.e. thermal conductivity, electrical resistivity, magnetoresistance, Hall coefficient and thermoelectric power. We discuss the implications of these measurements, particularly whether the observed behaviour can be understood in terms of conventional models, or whether radically new ideas are required. Since correlations between electrons are expected to be strong in these superconductors(4) it is not a priori clear how good band-theory calculations and the usual one-electron models are as a starting point for understanding their electronic structure and properties. A breakdown of the usual one-electron models could give important clues for the superconductivity. We also seek evidence regarding the importance of the electron-phonon interaction. These questions are of particular interest since the well-known resonating-valence-bond theory of Anderson et al.(5), and other theories, e.g. Lee and

Read(6), propose novel electronic mechanisms for superconductivity not based on the electron-phonon interaction, as well as novel interpretations of the resistivity above the transition temperature. Isotope effect measurements, which can indicate the importance of the electron-phonon interaction for superconductivity, have not been conclusive in the high-temperature superconductors, with early results indicating no effect in Y-Ba-Cu-O, but later results giving a significant effect in La-Sr-Cu-O, e.g. (7), and even some effect in Y-Ba-Cu-O(8).

We are led to propose that measurements on deliberately disordered superconductors could be of significance in helping understand the nature of the conducting mechanism and the origin of the superconductivity. These measurements should not be difficult to make, requiring irradiated or other disordered samples rather than single crystals. The basis of our analysis is a comparison of conduction above T_c in the high-temperature superconductors with that in other materials,in particular disordered metals.

A general comparison of the electrical resistivity of a typical high-temperature superconductor with that of other materials is shown in Figure 1. The resistivity above T_c is similar in magnitude to that of glassy metals, but the temperature dependence is much larger, reminiscent of that in crystalline metals. The new superconductors are close to the transition point at which a metal changes into a semiconductor - in fact in some samples the resistivity decreases with temperature above T_c as for the semiconducting polymer shown at the top of Figure 1. These features and others, and possible interpretations, are discussed below.

Thermal conductivity

An unexpectedly dramatic effect was discovered in the thermal conductivity of $YBa_2Cu_3O_7$(10), namely a strong increase below the superconducting transition temperature T_c, as shown in Figure 2. Typically for research on the new superconductors, the same effect was independently discovered by several other groups (11-14).

The thermal conductivity of superconductors normally decreases below T_c since the superconducting electrons cannot transport heat. However, it is not hard to find evidence that in Y-Ba-Cu-O, as in disordered metals, most of the heat current is carried by the phonons (lattice vibrations) rather than by electrons. Estimating the maximum size of the electronic component K_e of the thermal conductivity from the size of the electrical resistivity using the Wiedemann-Franz ratio, we find that K_e is only about 10 per cent of the total thermal conductivity at temperatures around 100 K figure 2). The sintered ceramic samples of the new superconductors do contain a substantial amount of disorder, but another major factor making the electronic contribution K_e small is the very small density of carriers (as shown by Hall effect and resistivity measurements discussed below). Quite apart from this argument, which assumes conduction by electrons or holes, the dominance of phonons in the thermal conductivity is demonstrated directly by its size and temperature dependence, which are closer to those of amorphous metals (in which phonon conduction dominates) than good crystalline metals (in which electronic conduction dominates).

Since paired electrons cannot scatter phonons, the heat current due to phonons increases in the superconducting state; this effect dominates over the decrease in the electronic component K_e of thermal conductivity if K_e is small. The only previous observations of an increase in thermal conductivity below T_c are for disordered alloys in which heat conduction by phonons also dominates over that by electrons (15). It is difficult to imagine circumstances in which the electronic system could give a large increase of K_e below T_c, even in strongly-correlated systems.

The observation of a peak in thermal conductivity of Y-Ba-Cu-O therefore leads fairly directly to an important conclusion. It provides strong evidence that a large fraction of the thermal resistivity above T_c arises from scattering of the phonons by electrons - otherwise little change would be seen below T_c when the scattering disappears. That the scattering of phonons by electrons and by disorder is comparable is very surprising, given the relatively large amount of disorder in these materials. It indicates a remarkably strong electron-phonon interaction. The only escape from this conclusion, assuming the electronic thermal conductivity K_e remains small below T_c, would be to find a mechanism whereby the phonon system itself shows a dramatic change as the temperature drops below T_c. This is not supported, however, by specific heat (16) and neutron measurements(17).

A La-Sr-Cu-O superconductor showed a much more muted effect, i.e. a possible bulge below T_c but no peak(10). Since the sizes of thermal conductivity, electrical resistivity and electronic thermal conductivity K_e are similar in La-Sr-Cu-O and Y-Ba-Cu-O, we conclude that the electron-phonon interaction is considerably greater in Y-Ba-Cu-O. It would seem rather surprising if this larger electron-phonon interaction did not contribute in some way to the extremely high values of T_c, although mechanism involving electron-electron interactions may also be needed in a successful theory.

We can make a rough estimate of the average phonon mean-free-path ℓ_{ph}, which indicates the distance the phonon moves between collisions, using standard expressions(18). For Y-Ba-Cu-O we find $\ell_{ph} \sim 25$. This mean-free-path is rather short, within an order of magnitude or so of typical interatomic spacings. It shows that the samples contain considerable disorder, as we deduced from the general size and shape of the thermal conductivity. Similar arguments apply for the La-Sr-Cu-O samples.

It is difficult to make any quantitative comment about the precise size of the electron-phonon interaction from the thermal conductivity, but we can check whether the ratio of thermal resistivity due to scattering of phonons by electrons to the electrical resistivity due to scattering of electrons by phonons is consistent with the usual expression for conventional metals. We find(18) that it is consistent if the density of carriers (i.e. electrons or holes) n is of the order of 10^{22} cm^{-3}. This seems a reasonable order of magnitude for n, being similar to but smaller than typical values for metals, and supports the applicability of the usual ideas of metallic conduction.

Electrical resistivity

The main features of interest in the resistivity, apart of course from the zero resistance state, are firstly the large size of the resistivity above T_c, and secondly the remarkably linear increase of resistivity with temperature in most samples (see Figure 3).

The interpretation of resistivity is a matter of controversy. Anderson et al.(5) suggested that conduction occurred by boson holes with very small residual resistivity owing to the difficulty of scattering the bosons, and with the linear law due to scattering by spinons. They quoted the lack of an extrapolated residual resistivity for good samples, as indicated by the dotted line in Figure 3, as confirming their model.

However, the extrapolation of the resistivity below T_c is not necessarily an extrapolation of the linear law as in the model of Anderson et al. A more conventional extrapolation according to the usual Bloch-Gruneisen function (14) is suggested by the dashed line in Figure 3. The upturn from the linear law at lower temperatures will be camouflaged in the region above T_c by superconducting fluctuations. In addition, the upturn could possibly be depressed to lower temperatures than $T_D/5$ (where T_D is the Debye temperature) as in the Bloch-Gruneisen law by the effect of disorder, of two-dimensional conduction, or of a phonon spectrum with more weight at low energies than for a Debye spectrum. In this conventional interpretation, we obtain large extrapolated residual resistivities of order 100 uΩcm even for samples in which the linear law extrapolates to near zero.

The plausibility of this interpretation can be tested as follows. The carrier density n and electronic mean-free-path ℓ required to give a residual resistivity of the order of 100$\mu\Omega$ in the conventional picture can be estimated approximately using the usual Boltzmann expression for conductivity. Of course, we are considering here averages over very anisotropic behaviour, and there is the complication in sintered materials that the real cross-section for conduction is significantly less than the geometrical cross-section of the sample (10,14). Nevertheless, the resistivity of single crystals along the direction of good conduction is similar to that seen in the sintered samples (22), so an order of magnitude estimate is of interest. For $\rho \sim 100 \mu\Omega$cm we find $\ell \sim 128$ A° for n~ 10^{21} cm^{-3}, or $\ell \sim 28$ A° for n~10^{22}cm^{-3}. These mean-free-paths are relatively short but not unusual in disordered materials.

We can also analyze the size of the linear resistivity slope at higher temperatures, using the expression of Allen et al. (23) for phonon-limited metallic resistivity (18). Using values of carrier density n between 10^{21} and 10^{22} cm^{-3}, the slope is accounted for if the product $m^*\lambda$, where λ is the electron-phonon coupling constant and m* the effective mass of the carriers, lies in the range 1 to 12. These values are consistent with a strong electron-phonon interaction and/or an enhanced mass, and show no conflict with the usual metallic conduction models.

A problem for the conventional interpretation of the linear resistivity law as arising from electron-phonon scattering, however, comes from the fact that the linearity appears to extend up to rather higher temperatures than expected, e.g. 1000 K for La-Sr-Cu-O (24). It is generally found that when the electronic mean-free-path ℓ decreases to the order of the interatomic spacing, the resistivity as a function of temperature shows a "saturation" effect, i.e. the increase of resistivity with temperature is reduced. Such an effect is thought to be seen in the A15 compounds. Gurvitch and Fiory (24) find that the resistivity of La-Sr-Cu-O shows no sign of saturation up to 4000$\mu\Omega$cm, in which case the estimated mean-free-path would be 3 A° for n~ 10^{21} cm^{-3} and less than 1 A° for n ~ 10^{22} cm^{-3}, the latter being less than the Cu-O bond length of 2 A°. Clearly a low density of carriers is required to account for the lack of saturation. But this means that the size of the slope of resistivity as temperature increases may be accounted for by rather low values of the electron-phonon coupling λ , if the estimate by Gurvitch and Fiory of the plasma frequency ω_p from measurements of the London penetration depth is correct. If the coupling λ were small in Y-Ba-Cu-O, however, it is difficult to see how the small number of electrons could scatter phonons as effectively as the large amount of disorder, which as we saw is required to account for the thermal conductivity peak.

The determination of the correct interpretation of the resistivity therefore requires further work. Complications of the resistivity analysis are the anisotropy and the nature of the sintered material, as mentioned, and also increases of resistivity due to loss of oxygen above 600 K in $YBa_2Cu_3O_{7-\delta}$. A masking of saturation effect by such an increase of resistivity in La-Sr-Cu-O remains a possibility. It would clearly be of great interest to force saturation by deliberately introducing additional disorder into the samples, to reach eventually a relatively temperature-independent resistivity with mean-free-path comparable to the atomic spacing, as in amorphous metals. The way electrical and thermal resistivity change upon strong irradiation of the samples should help clarify the extent to which conventional models for conduction are applicable.

We mention that as the Sr concentration in $La_{2-x}Sr_xCuO_4$ is reduced, the resistivity shows semiconducting rather than metallic behaviour and the superconductivity tends to disappear, as shown in Figure 4 for $x = 0.1$. In fact the resistivity at low temperature is in excellent agreement with the Mott variable-range hopping law for amorphous semiconductors (25). We discuss this case further in following sections.

Magnetoresistance

A magnetic field tends to reduce the superconductivity, giving rise to an increase in resistivity just above T_c as field increases due to the suppression of superconducting fluctuations. We have suggested(25) that magnetoresistance can be a sensitive probe of trace filamentary superconductivity, particularly in samples with semiconductor resistivity behaviour in which small changes of slope arising from superconductivity are difficult to see. We found superconductivity islands clearly revealed in magnetoresistance in the La-Sr-Cu-O sample with Sr concentration $x=0.1$, as the magnetic field suppresses the superconductivity below about 30K in a very similar fashion to the suppression of superconductivity above T_c in a zero-resistance sample (Figure 5). In contrast, the resistivity of the $x=0.1$ sample showed only a barely detectable anomaly near 30K (Figure 4).

Above 40 K, however, the magnetoresistance in both samples was less than one part in 5000. (These small values of magnetoresistance are typical of disordered systems, in which the deflecting effect of the magnetic field is very limited owing to the short electron mean-free-path). We are led to suggest 40 K as an upper limit for traces of superconductivity in the La-Sr-Cu-O system at normal pressure, in disagreement with suggestions of superconducting effects up to 100 K seen in thermopower, which are discussed below.

Hall coefficient

The Hall effect is the deflection of the charges carrying a current when a magnetic field perpendicular to the current is applied, the size of the effect being measured by the Hall coefficient R_H. The sign of R_H indicates the sign of the carriers, i.e. whether they are electrons or holes, and the size indicates their density, since for a single homogeneous band $R_H = (nq)^{-1}$, where q is the carrier charge. In metals, R_H is essentially independent of temperature for a single band, so temperature dependence is taken as a sign of multi-carrier conduction (e.g. conduction by electrons and by holes).

In the case of high-temperature superconductors, R_H is strongly temperature dependent (Figure 6), so no precise values of carrier density can be obtained. Although for a full description more complex models are required, we found (26) that the Hall coefficient of highly-doped La-Sr-Cu-O superconductors was consistent with the usual two-carrier model, with a hole density of a few times 10^{21} cm^{-3} and a smaller number of electrons. The temperature dependence of R_H can arise from different temperature dependences of the resistivities for each carrier group. A stronger scattering of holes than electrons by phonons relative to that by the disorder gives rise to R_H decreasing with temperature, as seen. Thus the observed behaviour is consistent with a strong hole-phonon interaction (holes are thought to be the carriers primarily associated with the superconductivity).

Although the Hall coefficient, like the resistivity, will be highly anisotropic, the data in Figure 6 are similar to those of Suzuki and Murakami (29) for a single crystal La-Sr-Cu-O thin film. In the sintered samples we see some average deviation over different directions, but this will be weighted very strongly in the direction of high conduction along the Cu-O planes. It is interesting to note that for this direction (but not in the poor conductivity direction) Allen et al. (30) predict a positive Hall coefficient from their band-theory calculations for $La_{2-x}Sr_xCuO_4$ for $x < 0.24$, in agreement with experiment.

Thermoelectric power

We come now to the least understood of the transport properties, but one that we argue is potentially rewarding. The thermopower is zero in a bulk superconductor because the superconducting pairs short out any thermoelectric voltage. Grant et al. (31) suggested that thermopower might be the transport measurement most sensitive to minute superconducting components in an otherwise normal sample. The reason is that thermopower arises from regions of the sample with a temperature gradient, so samples with disconnected superconducting filaments may have zero thermopower but finite resistivity (the argument is somewhat similar to that used (9) to explain why the thermopower of conducting polymers often shows more metallic behaviour than their conductivity). Grant et al (31) found that thermopower could be zero in sintered La_2CuO_4 at about 40 K even though resistivity was only just beginning to decrease. Further, they and Cooper et al (32) suggested that the decrease of thermopower beginning as temperature decreased below 90 K indicated trace amounts of superconductivity in nominally pure La_2CuO_4 with an onset temperature not much below 100 K.

However, these samples show a very large nearly constant non-metallic thermopower (200-300μV/K) at higher temperatures. For thermodynamic reasons, thermopower must go to zero at zero temperature, and a thermopower similar to that seen in La_2CuO_4 appears to be typical of systems near the metal-semiconductor transition (9). The interpretation of thermopower decreases as incipient superconductivity is therefore open to question, and as explained above, our magnetoresistance data suggest 40 K as the upper limit of superconductivity in the La-Sr-Cu-O system. A decrease of thermopower below 200 K is seen in our semiconducting $La_{1.9}Sr_{0.1}CuO_4$ sample (Fig. 4), but we interpret this as the behaviour of a normal material near the metal-semiconductor transition rather than an effect of incipient superconductivity.

Turning now to the highly-doped $La_{2-x}Sr_xCuO_4$ samples ($x>0.15$), we find that thermopower has much smaller values typical of metals as the resistivity becomes metallic. Some of our data are shown in Fig. 7; Chen et al (33) found similar results for La-Ba-Cu-O. We suggest that these data could be consistent with normal metallic thermopower, namely a phonon-drag peak dying out at higher temperatures to leave an approximately linear diffusion thermopower. If this interpretation is correct, the diffusion thermopower (at least in the most highly-doped specimens) is negative, as indicated approximately by the dashed line. The contrast with the positive Hall coefficient in the same samples mentioned above is surprising, yet this is just what is predicted by the band-theory calculations of Allen et al (30) for conduction along the Cu-O planes (the dominant conduction direction). The opposite signs of R_H and S can arise in situations with a complicated Fermi surface with different groups of carriers, because the weighting factors for combining thermopower and Hall coefficient contributions are different. In addition, thermopower sign is affected by the energy dependence of scattering. The success of the one-electron band theory suggests that, at least in this case, it could provide a reasonable starting point for the interpretation of the transport data, i.e. the electron-electron correlations are not sufficiently strong enough to invalidate it completely.

It should be noted that the diffusion thermopower sketched in Fig. 7 is non-linear (apart of course from its disappearance below T_c), because it is enhanced at low temperatures by the electron-phonon interaction derived by Weber (35). This effect is well-established in glassy metals in which phonon-drag is absent (36). When the electron-phonon interaction is strong, the knee at low temperatures is pronounced and the high-temperature thermopower does not extrapolate to the origin (34). Clearly if the large peak is phonon-drag and could be eliminated by increasing disorder, information about the electron-phonon interaction could be deducted from the remaining diffusion thermopower.

The data for $YBa_2Cu_3O_7$ (Fig. 8) are rather variable, even as to sign. This is partly because the thermopower is small, possibly signifying cancellation of different contributions. Some data sets, e.g. (10), suggests a small phonon drag peak, but the sharp peak of Mawdsley et al (37) just above T_c looks like a precursor effect of superconductivity instead. We have suggested mechanisms that could enhance phonon drag just above T_c (i.e. a decrease in effective carrier density and an increase in phonon current due to superconducting fluctuations), but the normal effect of superconducting fluctuations is to reduce thermopower as they short out the thermoelectric voltage.

There is a suggestion in some of the data sets that the thermopower extrapolates to positive values at zero temperature, as predicted (34) for the diffusion thermopower enhanced by the electron-phonon interaction (Fig. 9). However, no clear conclusions can be drawn from present data, particularly in view of the unexplained drop sometimes seen above about 240 K (according to the high-temperature data of Fisher (40), this decrease appears to continue up to about 600 K where a dramatic increase in thermopower begins).

Conclusion

Two of the key questions regarding the high-T_c superconductors are the mechanism of the superconductivity, and the applicability of the usual metallic models of conduction. Anderson et al. (5) start from the premise that these superconductors are so unlike those previously known that a wholly new theory is required. On the other hand, Salamon and Bardeen (42) conclude that there is nothing unusual so far except the value of T_c.

We have shown that the electron-phonon interaction is important in high-temperature superconductors, as demonstrated by the increased thermal conductivity just below T_c, especially in $YBa_2Cu_3O_7$. Data for the newer Bi and Tl based superconductors should prove most interesting in corroborating (or otherwise) this picture. If the larger thermopower peak around 70 K in La-Sr-Cu-O is indeed a phonon-drag peak, this also indicates a significant electron-phonon interaction. Other transport properties of highly-doped La-Sr-Cu-O and $YBa_2Cu_3O_7$ generally appear consistent with traditional metallic concepts with a very small carrier density. These observations are suggestive of a significant role for the electron-phonon interactions in the superconductivity, although electronic interactions (for example) would need to at least remove the usual Coulomb repulsion which oppose superconductive pairing to produce T_c values near 100 K. However, the apparent lack of saturation in the linear resistivity is a problem worthy of further investigation, and the thermopower of $YBa_2Cu_3O_7$ in particular is difficult to interpret.

While single-crystal measurements are undoubtedly of great interest, it seems to us that thermopower, for example, is likely to suffer from the difficulties of interpretation which have made it such a notoriously difficult property for metallic crystals.

We therefore point out the interest of data on deliberately disordered samples, where our experience in glassy metals (36) indicates that, if the new superconductors do indeed follow usual metallic behaviour, quantitative analysis should be possible. For Chevrel superconductors, this prescription works extremely well: as disorder scattering increases, excellent agreement with calculations is obtained (34), as shown in Fig. 9, favouring a traditional electron-phonon interaction in these materials compared to the more exotic model of Yu and Anderson (42). It would clearly be of great interest to check whether a similar simple pattern emerges in heavily disordered high-temperature superconductors. If it does not, a clear difference from the previous superconductors, and the importance of additional effects such as electron-electron correlations are established. If it does, information could be gained regarding the electron-phonon interaction. The enhancement effect would have to be considerably larger than in other materials if the electron-phonon interaction is a major cause of the high T_c value, as indicated in Fig. 9. If the giant defect-enhanced electron-phonon interaction proposed by Phillips (44) to account for the high-temperature superconductivity is correct, even more dramatic enhancements would be seen.

In addition, the observation of saturation in resistivity measurement on highly-disordered samples could help determine if the usual electron quasi-particle picture, which appears to account for many of the properties measured so far, breaks down. Thus further results on the transport properties, including an extension of the analyses discussed here to the Bi and Tl based superconductors, should be most helpful in resolving the present controversies.

Acknowledgment

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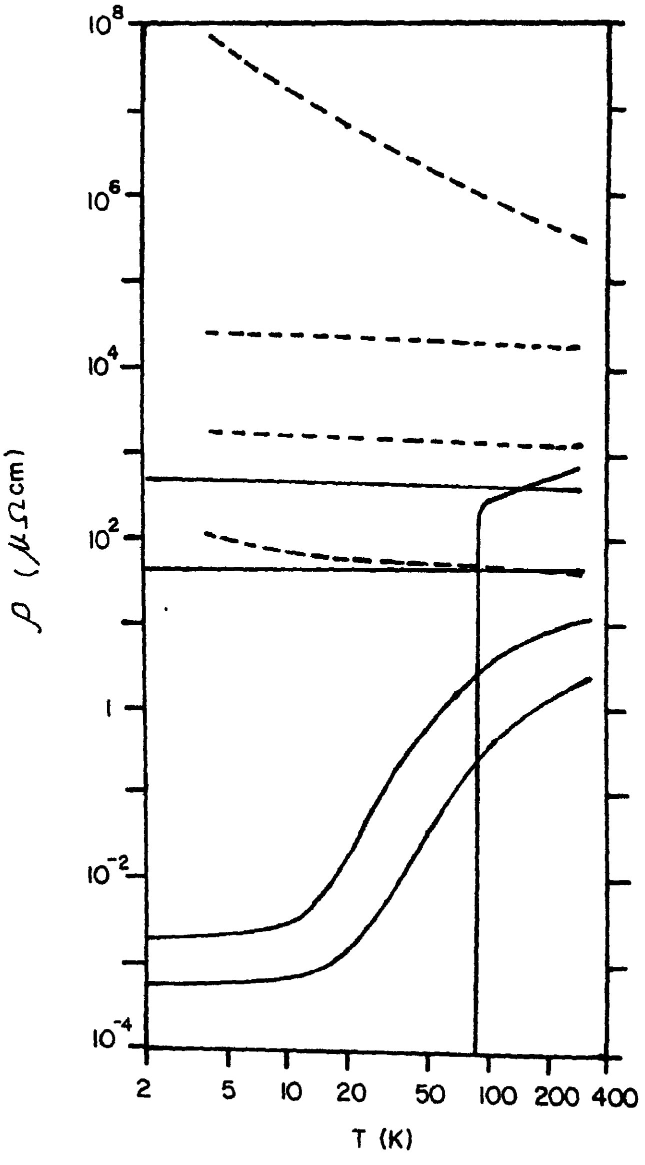

Fig. 1. Comparison of the resistivity of the high-temperature superconductor Y-Ba-Cu-O with that of the crystalline metals platinum (Pt) and copper (Cu), the glassy metal alloys Ca-Al and Mg-Zn, and conducting polymers (polyacetylene doped with I and $FeCl_3$) (9).

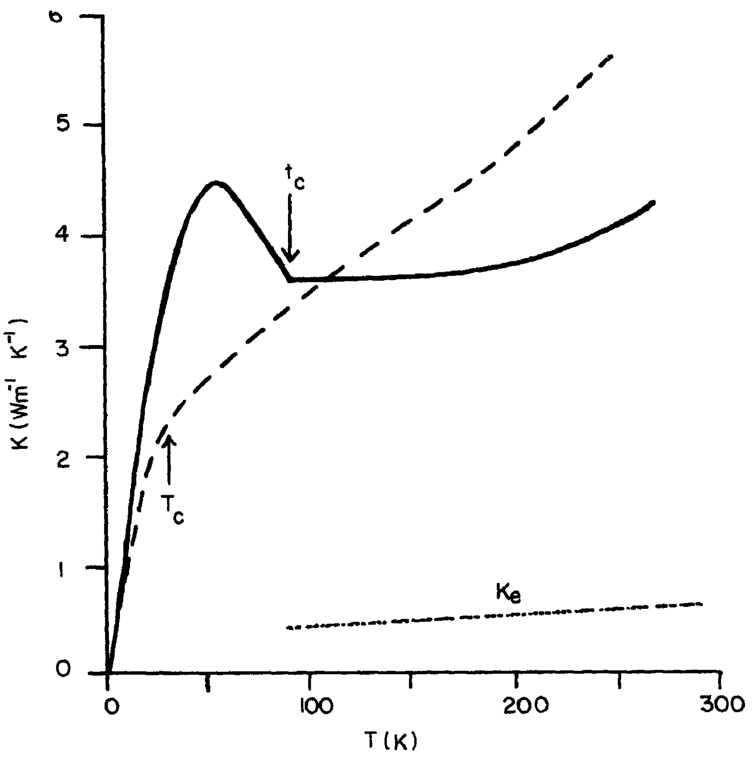

Fig. 2. Thermal conductivity K of $YBa_2Cu_3O_7$ (full line) and $La_{1.8}Sr_{0.2}CuO_4$ (dashed line) (10), with the dotted line showing the approximate maximum contribution of the electronic component K_e.

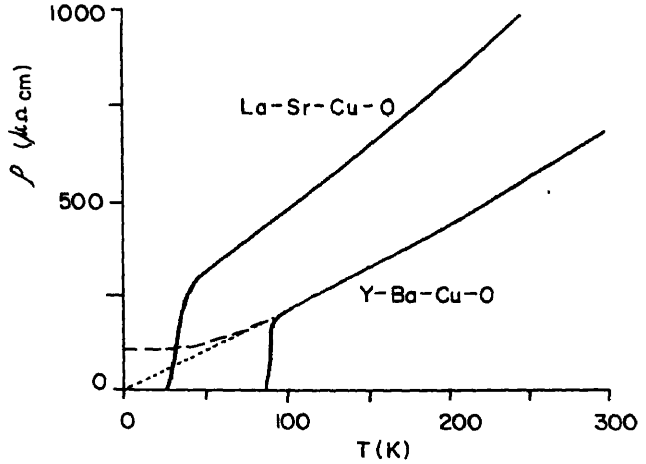

Fig. 3. Resistivity of $La_{1.8}Sr_{0.2}CuO_4$ (19) and a sample of $YBa_2Cu_3O_7$ in which the linear law "extrapolates" to the origin (20). The dotted line shows the extrapolation of resistivity below T_c suggested by Anderson et al. (5), while the dashed line shows the conventional extrapolation the temperature dependent contribution arises from scattering by the carrier-phonon interaction.

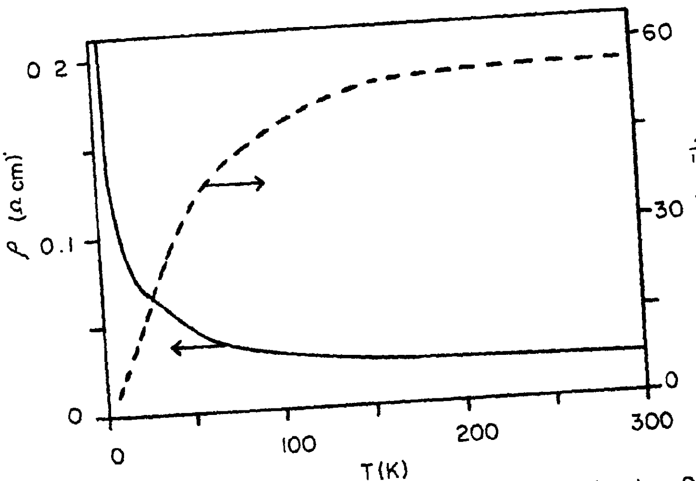

Fig. 4. Resistivity ρ and thermoelectric power S of a semiconducting $La_{1.9}Sr_{0.1}CuO_4$ sample (25).

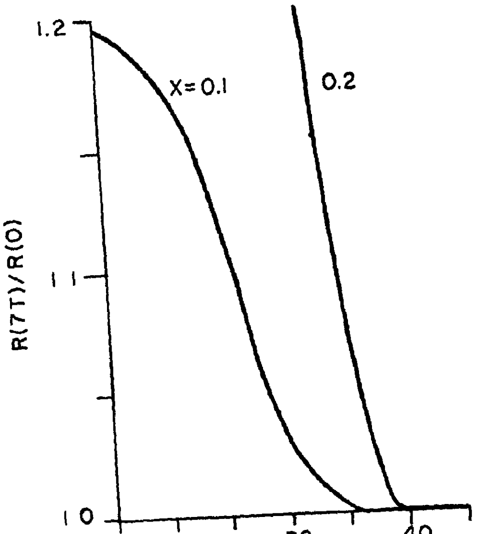

Fig. 5. Magnetoresistance of the $La_{2-x}Sr_xCuO_4$ (x=0.1) sample showing the large effect below 35K which reveals the presence of superconducting filaments, compared to data for a superconducting sample (T_c ~ 30K, x = 0.2) (25). R(7T) is the value of the resistance in a field of 7T.

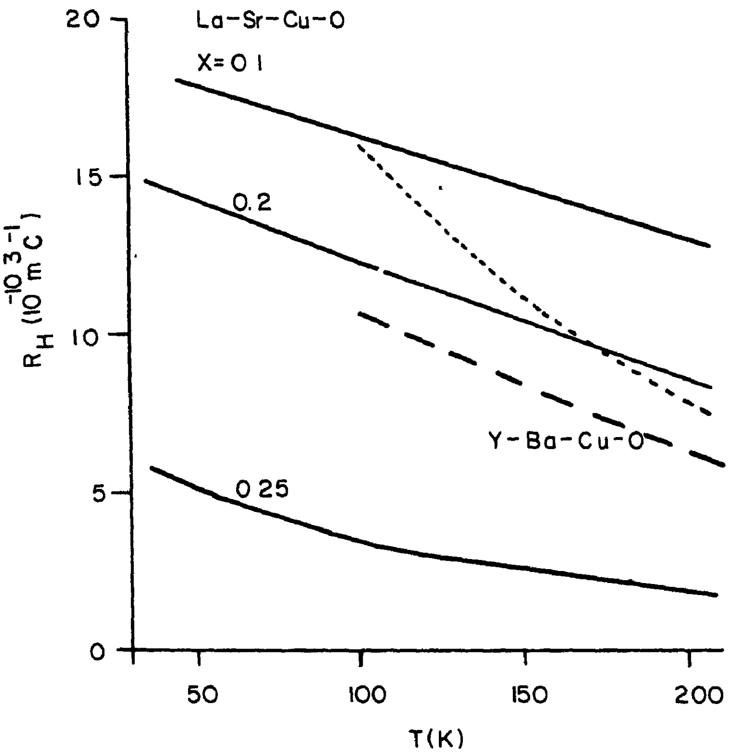

Fig. 6. Hall coefficient for $La_{2-x}Sr_xCuO_4$ for x = 0.15 (27), x = 0.2 and 0.25 (26), and for two samples of $YBa_2Cu_3O_7$ from (13) (lower dashed lines) and (28) (upper dashed line).

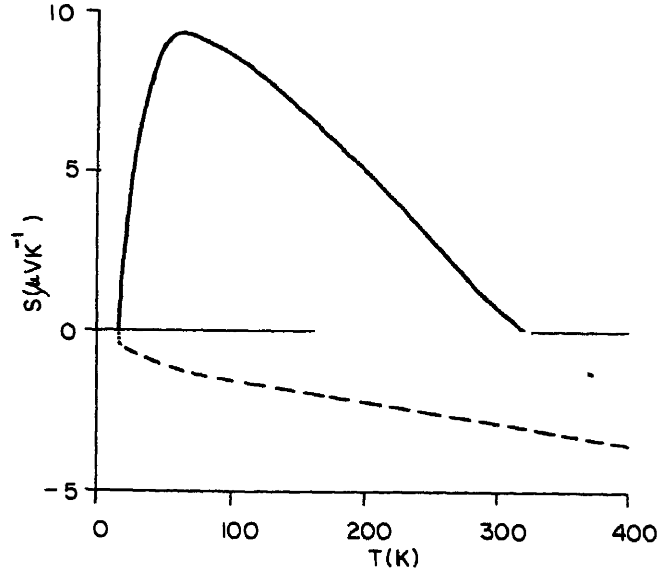

Fig. 7. Thermopower of $La_{2-x}Sr_xCuO_4$ x = 0.25 (19). A possible interpretation is a negative diffusion thermopower (dashed line) and a large positive phonon-drag peak. The diffusion thermopower has a knee due to electron-phonon enhancement at lower temperatures (34).

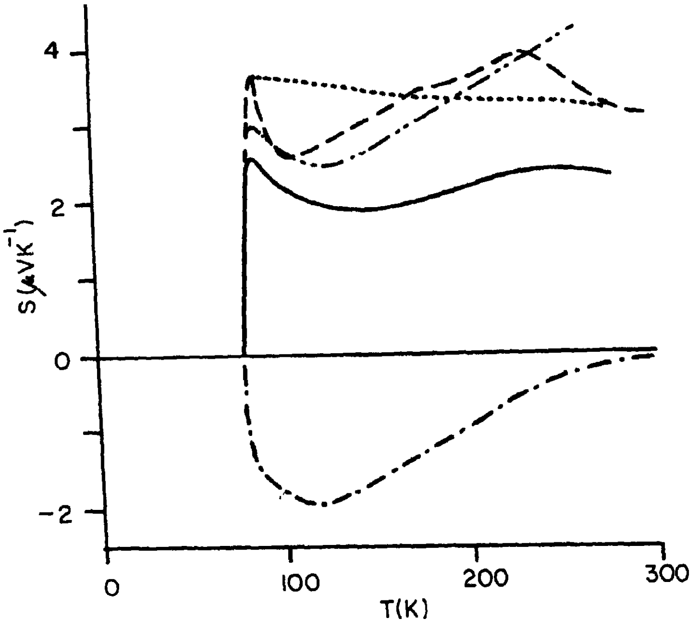

Fig. 8. Some thermopower data for $YBa_2CuO_3O_7$, from (10) (dots), (37) (dashed line), (38) (dotted line), (14) (double chained line).

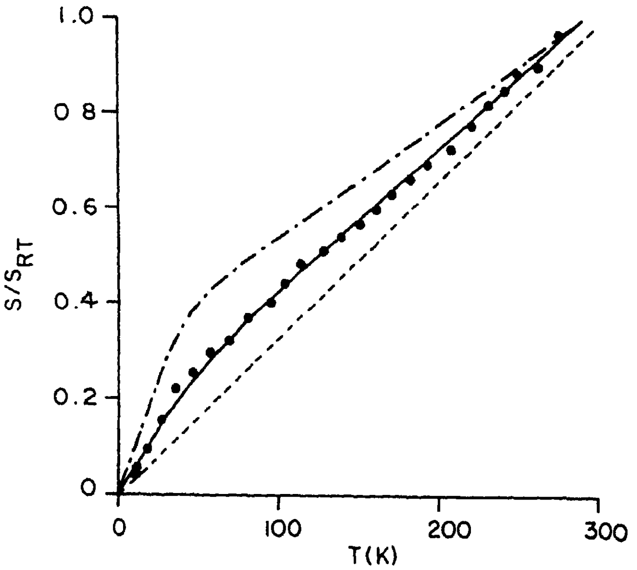

Fig. 9. Comparison of experimental points (dots) from (41) with theory (full line) (34) for the thermopower of the disordered Chevrel superconductor $Cu_{1.8}Mo_6S_5Te_3$. The thermopower enhancement, i.e. the deviation above the straight line, is calculated without adjustable parameters. S_{RT} is the room-temperature value of thermopower.

High temperature superconductors: problems of current transport for large current applications

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Abstract

Large scale utilization of high temperature superconductors necessitates that they should carry acceptable critical current densities in high magnetic fields. The ceramic superconductors are extreme type-II superconductors whose Jc is determined by vortex pinning. Some elementary aspects of the problem of current transport are examined and the situation for high temperature superconductors is assessed.

Introduction

With the advent of high temperature superconductors in 1986 the whole scenario of superconductivity has now undergone a dramatic change. Right since the discovery of superconductivity in 1911, despite very extensive efforts primarily centered around metallic materials synthesized in various forms, under varied experimental conditions and possessing different crystallographic structures, the rate at which Tc rose remained disappointing (Fig.1). Indeed, until 1973 the highest reported value of the critical temperature Tc below which superconductivity occurred was confined to 23.2 K, for an intermetallic compound Nb_3Ge and this mark could not be surpassed during the next 13 years. In the wake of this Bednorz and Muller's (1) discovery in every sense was an undisputed breakthrough. They showed that the mixed metal oxide La-Ba-Cu-O, a ceramic material, to become superconducting at a much higher Tc of about 30 K. It was not just the rise in the critical temperature that mattered, although by itself it was something quite extraordinary. More than that it was the breakthrough in the type of materials that were being investigated. No one with any kind of empirical perception had ever considered ceramics to be the candidates for high Tc. The interest was immediately shifted from metallic systems to ceramic cuprates and within months of Bednorz and Muller's discovery came the exciting announcement of Y-Ba-Cu-O system by Chu and his collaborators (2) exhibiting superconductivity at about 90 K. This became the first superconductor at liquid nitrogen temperature of 77 K. Interestingly, in this system when Y was substituted by other rare-earths like Dy, Er and Ho which are known to carry magnetic moment, the Tc, surprisingly, remained practically unaltered. The exciting developments continued and the beginning of 1988 saw two more systems namely Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O [3,4] getting added to the liquid nitrogen temperature superconductors which had Tc values in the range of 85 to 125 K, depending on the stoichiometry and processing conditions used.

The metallic superconductors which had been in existence for the last over 75 years, necessitated the use of expensive liquid helium at 4.2 K. Both the cost economics and the constraints involved in using liquid helium and working at such low temperatures were the prime deterring factors preventing their extensive utilization and, consequently, superconductors found a place only in restricted and rather selective applications. For the same reasons, scientific research in this area too remained a preserve of a somewhat limited number of laboratories and institutes who could afford helium liquefaction and gas recovery systems. The discovery of superconductivity at liquid nitrogen temperature has however changed the situation drastically. It has brought the experimental superconductivity research within easy reach of low budget laboratories all over the globe which would undoubtedly speed-up the technological advancement. Likewise, it has opened up exciting prospects of a whole lot of industrial applications ranging form ultrafast minicomputers to gigantic fusion reactors, all functioning at far lower costs at liquid nitrogen temperatures.

Various laboratories in India, such as Indian Institute of Science, Bangalore, Tata Institute of Fundamental Research, Bombay, Bhabha Atomic Research Centre, Bombay, National Physical Laboratory, New Delhi and Indian Institute of Technology, Madras spared no time to reconfirm the findings of the original discoveries. Some of the important results such as the identification and crystal structure of 90 K phase in the yttrium system, presence of weak links and Josephson currents, variance of Tc with rare-earth dopings, realization of a stable Tc of 106 K in carefully processed yttrium compound and the possible presence of extra high Tc close to the room temperature were obtained either at par with or even somewhat ahead of the reports coming from abroad. Appreciating this and realizing the scientific and technological importance of high temperature superconductors, the Government of India formed an Apex Body with the Prime Minister as Chairman and created a Program Management Board to plan and promote both basic and applied research in the newly emerged frontal area. As a result of this about 50 R & D laboratories, universities and Institutes of Technologies all over the country are presently involved in doing different aspects of pure and applied studies on high temperature superconductors.

While the basic research in India and elsewhere is primarily directed to find the answer of the ultimate question of the mechanism of high Tc, the applied studies are focussed on the utilization of the high temperature superconductors in small and large scale applications. The small scale applications are basically thin films devices like SQUIDs, computer elements and quiterons which are mostly small current applications. Large scale applications are mainly based on long lengths of wires, tapes or cables which are meant to carry large transport current either as electromagnets or for power transmission. It is well realized that the development of electromagnet of high temperature superconductors operating at liquid nitrogen temperature would perhaps constitute the major technological feat having a revolutionary impact on various sectors like power engineering, medicine, high speed magnetically levitated transport, high energy nuclear applications etc. This is simply due to the fact that electromagnets form the major part of electric motors, generators, MHD energy conversion, for magnetic confinement of plasma in fusion reactors, energy storage, NMR whole body imaging, nuclear bubble chamber, particle accelerators, etc. Superconducting magnets, because of their zero resistance, offer unique advantages over conventional electromagents. Firstly they have practically no power dissipation. They can be energized by simple power supplies and the circulating currents can be readily switched into persistent mode so as to create a permanent magnet system no longer requiring external power supply. Even for superconducting magnets operating at liquid helium temperature there is a power saving by a factor of 100 at a field of 10 T. Moreover, owning to much larger current densities available the overall size of the system is substantially reduced.

The current transport in the ceramic superconductors however poses a serious problem that their critical current density is very low. In this chapter we will examine the problem of critical current of high temperature superconductors.

Critical current

Critical current stands for the maximum lossless current that a superconductor can sustain before the voltage develops. The critical value is generally taken as that at which the transport current gives rise to a voltage of about 0.1 to 1 microvolts over 1 cm length of the wire. It is generally denoted by the parameter Ic while the critical current density is represented by Jc. Because of this, whenever a new superconductor is discovered, Ic or Jc is the most sought after parameter and its enhancement has generally posed a considerable challenge.

Critical current of pure elements

When Onnes (5) discovered superconductivity in Hg in 1911 and in Pb and Sn in the subsequent years he could readily visualize their tremendous potential for making very powerful electromagnets which would carry unlimited electric currents without any Joule dissipation. However, to his great disappointment he found the phenomenon to abruptly disappear in the presence of a magnetic field when the latter exceeded a certain critical value less than a few hundred oersteds. Silsbee, in 1916 (6), showed that essentially the same effect resulted with the passage of a transport current of a critical magnitude. The critical current being that which produced the critical magnetic field, known as the bulk or thermodynamic critical field Hc, on the surface of the wire, i.e.,

$$\frac{2\,Ic}{a} = Hc \qquad \ldots (1)$$

This is equivalent to a maximum or depairing current density $Jd = Hc/4\lambda$ which flows over the penetration depth λ . Eq. (1) is Silsbee's rule. Since Hc for pure elements is small, less than a few hundred oersteds, pure metals like Nb, Pb or Sn are of no use for making superconducting high field magnets, although owing to their relatively small penetration depth their zero field depairing current density Jd is indeed very large.

During 1928-29, de Haas and Vooged (7) at Leiden had found for some Pb-Bi alloys a field of 25kOe (2.5 T) was necessary to quench superconductivity. But a solenoid of this alloy proved disappointing as the wire could not carry current anywhere near that expected from Silsbee's rule. This could not be understood as magnetization studies of even pure elements, let alone of alloys, had not even seriously started at that time.

Type-I and Type-II superconductors

Discovery of Meissner Effect (8) came in 1933 which showed that in the presence of a small magnetic field the transition from normal to superconducting state took place with complete expulsion of magnetic flux (Fig. 2) from the bulk of the sample, i.e., B = 0. In pure metals such a state of complete diamagnetism persisted until the external field reached the thermodynamic critical value Hc when abrupt field penetration occurred and the material reverted to normal. Studies on alloys, which began many years later, on the other hand, showed a significantly different behaviour. Here, the Meissner effect and the ideal diamagnetism was in general observed only until a much lower field, which came to be known as "the lower critical field, HcI", beyond which the field penetration was gradual and it continued until a much higher critical field, known as "the upper critical field, Hc2", when bulk of the material turned normal. A detailed theory of this type of magnetization behaviour was given in 1957 by Abrikosov (9) by extending the phenomenological theory of Ginzburg and Landau (the G-L theory) (10) for the situation where the penetration depth λ is greater than the range of coherence ξ. λ measures the exponential field penetration which is essentially the distance over which the shielding super-currents flow, while ξ is the length over which any perturbation in the superconducting order is smoothened out. For pure elements, know as type-I superconductors, $\lambda < \xi$ and the surface energy between the normal and superconducting domains is positive and their magnetization behaviour is as shown in Fig. 3. The effect of alloying is to decrease the electron mean free path resulting in increase in λ and decrease in ξ. If $\lambda > \xi$, the surface energy becomes negative with the result that at a field HcI<HcII the field penetration becomes energetically favourable resulting in the characteristic type-II behaviour of Fig. 4.

The G-L theory gives a dimensionless parameter k, known as the Ginzburg-Landau parameter, which is equal to

$$k = 2\sqrt{2}\; e\, Hc\, \lambda^2/\hbar c \qquad \text{... (2)}$$

For a type-I supeconductor $k < 1/\sqrt{2}$ while for a type-II, $K \gg 1/\sqrt{2}$ this parameter can also be expressed as $k = Hc2/\sqrt{2}$; $Hc = 1/\sqrt{2}\,\lambda/\xi$ For a type-II superconductor the parameter Hc is essentially hypothetical which can be determined by measuring the area of a reversible magnetization curve. It is also a measure of the condensation energy per unit volume of the superconducting state, given by $Hc^2/8\pi$ such that

$$\int_0^{H_c^2} MdH = H_c^2/8\pi \qquad \text{... (3)}$$

Mixed state

Between Hc1 and Hc2 a type-II superconductor is in the mixed state, first described by Abrikosov in 1957. The field penetration in the mixed state occurs in the form of a triangular lattice (termed as flux line lattice FLL) of flux vortices. A flux vortex comprises of a normal core of radius ξ carrying a quantum of magnetic flux ϕ_0 equal to 2×10^{-7} G cm^2 surrounded by vortices of supercurrent spread over a distance λ (Fig. 5). At hcI the first flux vortex is nucleated and with increasing field their equilibrium separation is reduced such that at Hc2 the normal cores begin to overlap and thus bulk of the material turns nonsuperconducting.

Critical current in mixed state

Commercially, the most attractive property of a type-II superconductor is its large upper critical field and it is this property which results in superconducting electromagnets producing high magnetic fields without losses. However for this application a superconducting wire is not only required to have a large Hc2 but it must also possess the ability to carry an appreciably high magnetic field. The resistance-less current in a homogeneous type-II superconductor is limited to that value which just produces the field Hc1 at its surface, as given by Silsbee's rule. Above Hc1 the sample contains both the transport current and magnetic vortex lines threading through bulk of the sample. Their coexistence results in what is known as the Lorentz driving force $1/C\,(\bar{B} X \bar{J})$ acting on flux vortices, where J is the current density and B is the average magnetic induction. This force is maximum when transport current is transverse to the magnetic field and it acts on flux vortices, tending them to move. The situation for a longitudinal magnetic field is somewhat complicated. Flux vortices take up helical configuration and in doing so reduce the Lorentz force. This 'force free' configuration results in much higher Jc values than in the transverse case.

In a homogeneous wire there is no counteracting force preventing this, and an unstable situation therefore results in which the flux vortices are driven into motion. Such a motion is a dissipative process giving rise to resistance and flux vortices must be pinned so that their motion is inhibited. Various kinds of inhomogeneties such as lattice defects, second phase, composition influctuations in the material etc., can interact with flux lines and produce pinning forces which counteract the Lorentz driving force and promote a nonequilibrium vortex distribution. The mixed state can now carry lossless transport current upto a maximum or critical value which corresponds to the driving force being just equal to the pinning force. As inhomogeneties are progressively added the critical currrent increases and the magnetization curve becomes more and more hysteretic; the two effects being closely related (Fig. 6).

Driving force

In the isothermal situation the driving force on a flux line in a static nonuniform configuration of curved vortices is given by (11)

$$f_L = \frac{\bar{\phi}_o}{4\pi} \times \text{curl}\ \bar{H}(\bar{B}) \qquad \ldots (4)$$

which for a two dimensional system of straight flux lines reduces to

$$f_L = \frac{\phi_o}{4\pi} \quad \frac{dH(B)}{dx} \qquad \ldots (5)$$

where $\bar{H}(\bar{B})$ is the external field in equilibrium with the local induction B. For $H \gg H_{c1}$, $H(\bar{B}) = \bar{B}$. The above expression is nothing but $1/C\,(\bar{B} \times \bar{J})$. In an ideally homogeneous superconductor, under the action of the driving force a non-uniform vortex distribution is unstable and the flux vortices move so as to make the flux gradient zero. In real materials, inhomogeneties offer pinning forces, counteracting the driving force, and a static non-uniform vortex distribution becomes permissible, provided $F_L < F_p$, where F_p is the maximum pinning force per unit volume. The equation

$$\frac{B}{4\pi} \quad \frac{dB}{dx} = -F_p \qquad \ldots (6)$$

defines the critical state (12) where the field gradient is maximum or critical and it corresponds to the critical current density Jc at induction B. A greater Fp implies a steeper flux gradient and a higher Jc. Thus, if field dependence of Jc is known, the field profile in the superconductor can be determined from which the magnetization curve the field dependence of Jc can be estimated. With high temperature superconductors this latter approach is particularly popular for determining Jc as the method is free from the constraints of making low resistance contacts needed for transport Jc measurements.

Role of inhomogeneties, flux pinning

Clearly, for a superconductor to sustain a large transport current density in the mixed state the flux vortices, or more correctly the flux line lattice-FLL must be pinned. The pinning can occur through their interaction with various types microstructural inhomogeneties, such as dislocation networks, different types of inter and intra-grain boundaries, composition fluctuations, precipitates of a second phase etc. They give rise to local variations in superconducting properties where the flux line energy is locally reduced to get pinned. A flux vortex has basically two components contributing to its line energy: (i) the normal core of radius ξ and (ii) vortices of circulating supercurrents spread over a distance λ. The former leads to the 'magnetic interaction'. Generally magnetic pinning is more important in low-k materials.

The interaction between an isolated defect and FLL results in the elementary pinning force f_p which when properly summed over all the pinning entities per unit volume, taking into account the elastic properties of the FLL, gives rise to the volume pinning force Fp, mentioned earlier. The critical current is defined by the force balance equation

$$\bar{F}_L = \frac{1}{C}(\bar{B}x\bar{J}) = -\bar{F}p$$

Depinning of flux vortices

When the driving force just exceeds the pinning force the depinning occurs and the current reaches the critical value. Depinning process can be acelerated by thermal activation. At any finite temperature T < Tc, thermal activation aided by Lorentz driving force can cause pinned flux lines to hop out of the free energy wells of depth Eo, (the pinning energy) and produce dissipation even when $F_L < F_p$. This phenomenon is known as the 'flux creep' (Fig. 7). As a result, at a relatively lower value of the driving force depairing effect can become detectable, giving (13)

$$(F_L)_{Critical} = 1/C\,\bar{B}xJ_c = 1/V_x\left[E_o - K_BT\ln R_o/R_c\right] \qquad \ldots(7)$$

However, when T is small and Eo is large the factor $K_BT\ln(R_o/R_c)$ is negligibly small and the creep effect is not very important. However, when Eo is small and T is large, the flux creep can be quite relevant in reducing Jc.

High temperature superconductors

Anisotropy aspects

During last 12 months both La-Sr-Cu-O and Y-Ba-Cu-O and their related other systems have been extensively studied for their magnetization and critical current behaviours. Both are extreme type-II superconductors with their k = 100 and $\lambda \gg \xi$. There is a considerable scatter in the reported data for various parameters, but tentatively some of the parameters may be given as below:

	La-Sr-Cu-O	Y-Ba-Cu-O
ξ (o)	25 A°	15 A°
λ (o)	2500 A°	1400 A°
Hc(O)	4.5 kOe (0.45T)	8 to 13 kOe (0.8 to 1.3T)
Hc2(O)	650 kOe (65T)	1000 to 1800 kOe (100 to 180T)

Even larger values of Hc2 have been reported for single crystal samples when measurements are made parallel to a-b plane. The critical field is several times smaller when measured perpendicular to a-b plane. The anisotropy is closely linked with their unusual crystal structure, (Fig. 8a and b) in particular large c-parameter and the presence of highly conducting Cu-O networks along a-b plane. The situation holds also for Bi and Tl based ceramic superconductors. It can be readily seen that,

$$\frac{HC_2^{\parallel}}{HC_2^{\perp}} = \frac{\xi^{\parallel}}{\xi^{\perp}} = \left(\frac{\rho_n^{\perp}}{\rho_n^{\parallel}}\right)^{1/3}$$

In the case of $YBa_2Cu_3O_{7-\delta}$, known as the 123 compound, the anisotropy in resistivity, $\rho_n^{\perp}/\rho_n^{\parallel}$ is found to be about 250, giving anisotropy factor in the upper critical field to be about 6.

Critical parameters

In the table below, the characteristic parameters of 123 compound are compared with some of the important conventional high field superconductors (14)

	Nb3Ge	**PbMo6S8**	**MoRuPB**	**YBaCuO**
Hc2(O)	340 kOe	550 kOe	180 kOe	1200 kOe
Hc(O)	4 kOe	1.5 kOe	1.2 kOe	10 kOe
λ(O)	3500 A°	4000 A°	3500 A°	1400 A°
ξ(O)	35 A°	25 A°	50 A°	10-30 A°
Jd(O)	8X10^7 A/cm^2	3X10^7 A/cm^2	2X10^7 A/cm^2	6X10^8 A/cm^2
Jc(4K, O H)	7X10^6 A/cm^2 (Nb3Sn)	2X10^5 A/cm^2	10^5 A/cm^2	2X10^7 A/cm^2 (Thin Films) 2X10^6 A/cm^2, 77K (Thin Films)
Jc(4K, 5T)	4X10^6 A/cm^2 (Nb3Sn)	10 A^4/cm	10^3 A/cm	1.5X10^4 A/cm^2 (sintered compact)

It is clear, that a high upper critical field alone is not enough to make the material technologically attractive. Both PbMo6S8 and MoRuPb (as metallic glass) did not succeed because of their disappointing Jc. The pinning entities in the former are too course in relation to its coherence length while in the latter they are relatively too fine for realizing effective pinning. As may be seen YBaCuO has the highest depairing current density Jd(O), and the zero field Jc values at 4 K for deposited thin films are about an order of magnitude close to Jd(O). But, the sintered compacts have Jc values two to three orders of magnitude lower. To date, the highest zero field Jc at 77 K of the material sintered and heated above its melting temperature is 1.7X10^4 A/cm^2m which is quite low for the magnet application. The bulk single crystals are found to possess Jc values intermediate between thin films and polycrystalline sintered compacts.

Nature of flux pinning

Low Jc(H) values suggest that bulk pinning in these materials to be low, and the conventional defects like twin boundaries, grain boundaries etc. which are present in abundance are not providing effective pinning. In these systems the FLL is extremely stiff and is therefore more difficult to pin.

Some of the broad features of the measurements made on YBaCuO in the form of polycrystalline sintered compacts, bulk single crystals and thin films (Figs.9-11) may be mentioned. The data given are of various workers details of which may be found elsewhere(15).

[1] The general scaling law for the volume pinning force, given by $F_p(b,T) \propto Bc2(T)^m \ b^n \ (1-b)^{\lambda}$ where b=B/Bc2(T) and m = 2.5, n = 0.5 and λ = 2 does not seem to hold. (Bc2 is essentially same as Hc2).

[2] In the measured field interval upto 5 or 6T or more, contrary to the decrease exhibited by conventional superconductors, Jc(B) either remains constant or even slightly increases with field.

[3] Decrease of Jc with increasing T is much stronger for polycrystalline samples than for the usual type II superconductor. The exponent m is much larger, i.e. 4 to 6 instead of 2 or 2.5 found for the conventional superconductors. The bulk single crystals, on the other hand, have m close to 2.5.

[4] The pinning curves for bulk single crystals show the existence of maxima in Fp(B) at very low values of b_m less than 0.02 or they give indication of rather broad maxima in polycrystalline samples. The maxima tend to shift to a higher b_m value as the temperature is lowered.

[5] Some data have given indication of Jc decreasing exponentially with H. The observed magnetization curves fit very well with the exponential field dependence.

[6] Zero field Jc values of epitaxially deposited thin films have high Jc values but in many instances Jc is found to decrease fast, almost exponentially, with H. More recently, however, when the deposited film is of HoBaCuO and formed with an orientation (16) such that a and b axes respectively lie perpendicular and parallel to the plane of the film, the measured Jc values upto a field of 1.5T continue to be commendably high, about $10^6 A/cm^2$.

Many of the above findings suggest that in sintered compacts the pinning at $T<Tc$ is provided by intergrain connections serving as proximity type of pinning centres; the proximity connections being in the dirty limit (15). This way one can tentatively understand why over a field range Jc increases with H. The number of effective pinning centres increases with decreasing temperature. At T close to Tc, the current is essentially weak-link like. The exponential decrease of Jc with H reported for some of the bulk as well as thin film specimens may be taken indicative of the dominance of surface pinning and near absence of bulk pinning. In suitably oriented films containing Ho, mentioned above (Fig. 10), Jc is high and is much less sensitive to Jc, the effect is attributed to a larger coherence length in a-b plane along which the current flows and intergrain weak links are thus not so effective. Jc is therefore no longer strongly sensitive to the imposed field and high values upto a field of 1.5T could either be due to strong surface pinning effect as recently suggested by Takacs (17) or may be ascribed to favourably aligned defects like twin boundaries or grain boundaries providing more effective bulk pinning (18). As compared to the thermodynamic critical field, Hc, the field of 1.5T is not too large and therefore Jc values at much higher fields would confirm whether it is the surface pinning effect or is caused by bulk pinning.

The problem of Jc and flux pinning in high temperature superconductors however remains way away from being understood. A systematic study of microstructure, magnetization and Jc on well characterized single crystals would go a long way towards realizing acceptable Jc values in high magnetic fields which is the prime requirement for the majority of large scale engineering applications.

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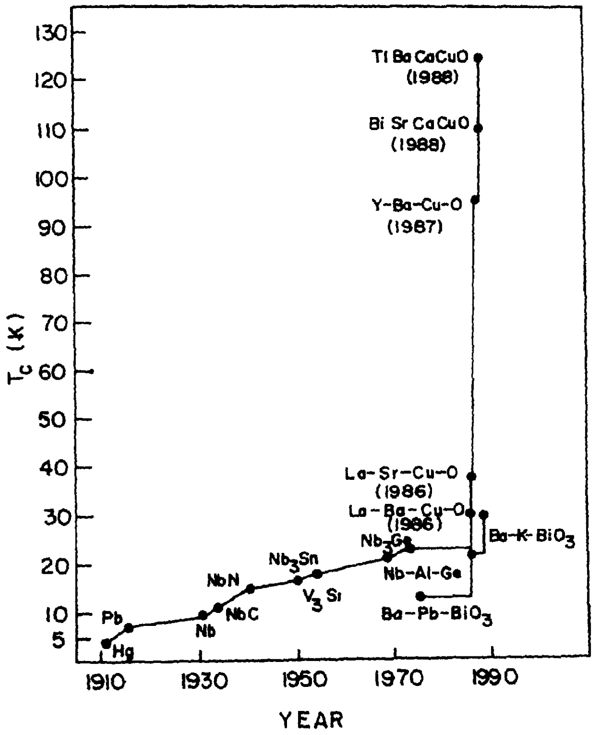

Fig. 1. Increase in the critical temperature since the discovery of superconductivity.

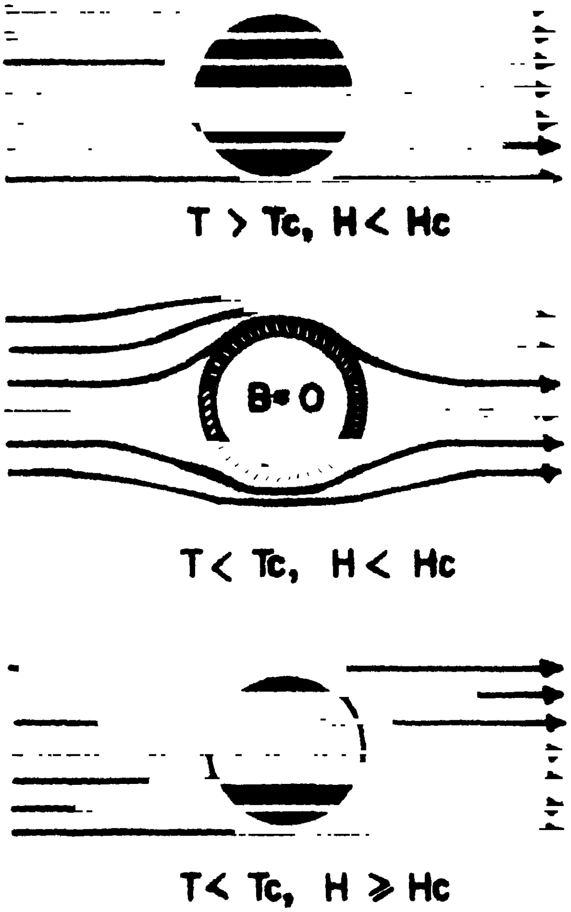

Fig. 2. Meissner effect.

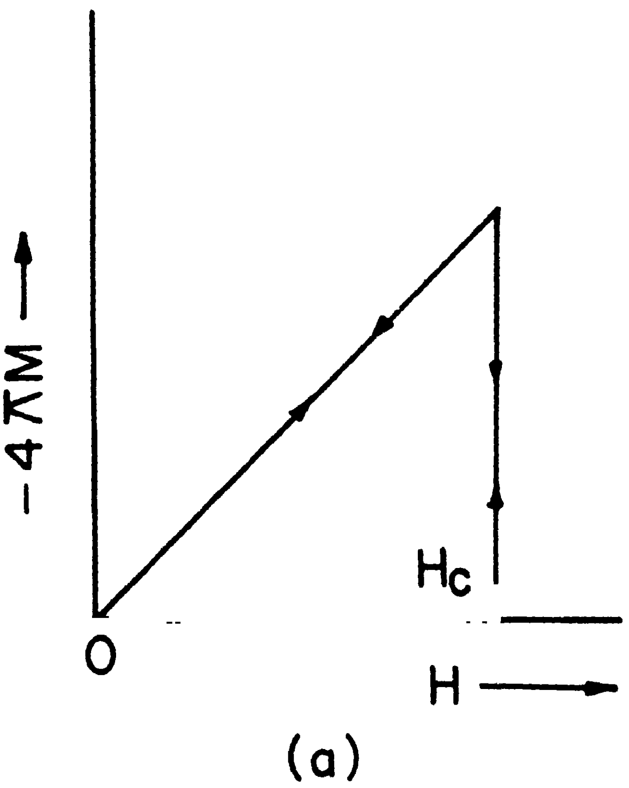

Fig. 3. (a): Magnetization

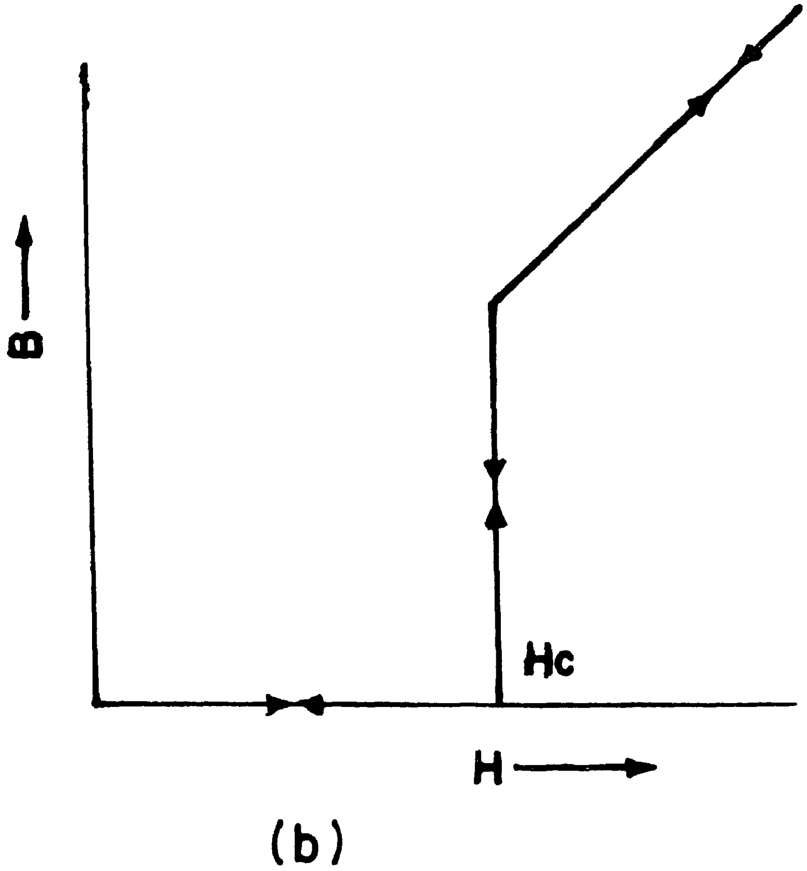

Fig. 3. (b) B-H curves for a Type-I Superconductor.

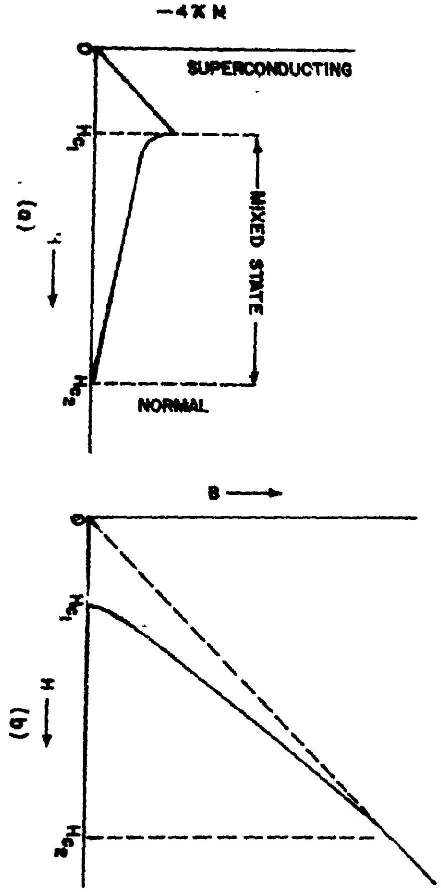

Fig. 4. (a): Magnetization

(b) B-H curves for ideal Type-II Superconductor.

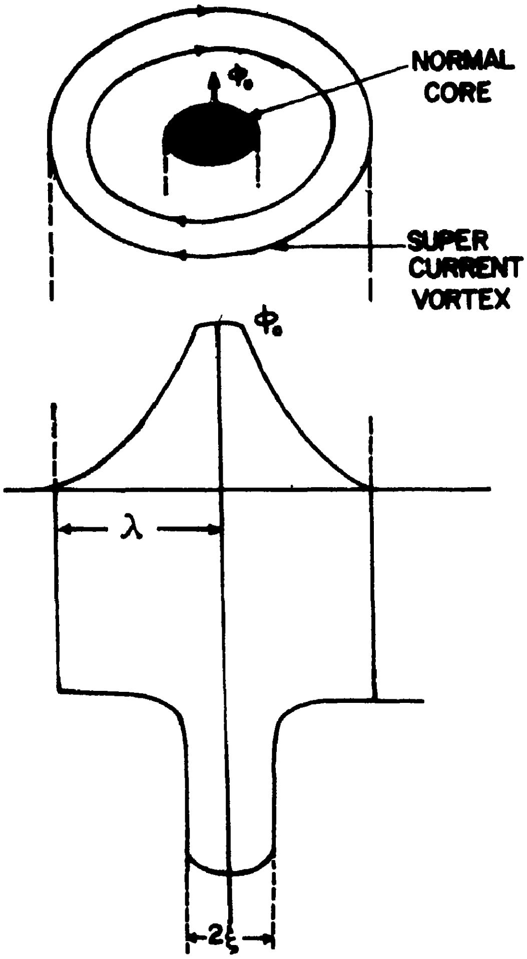

Fig. 5. Structure of an Abrikosov's vortex line.

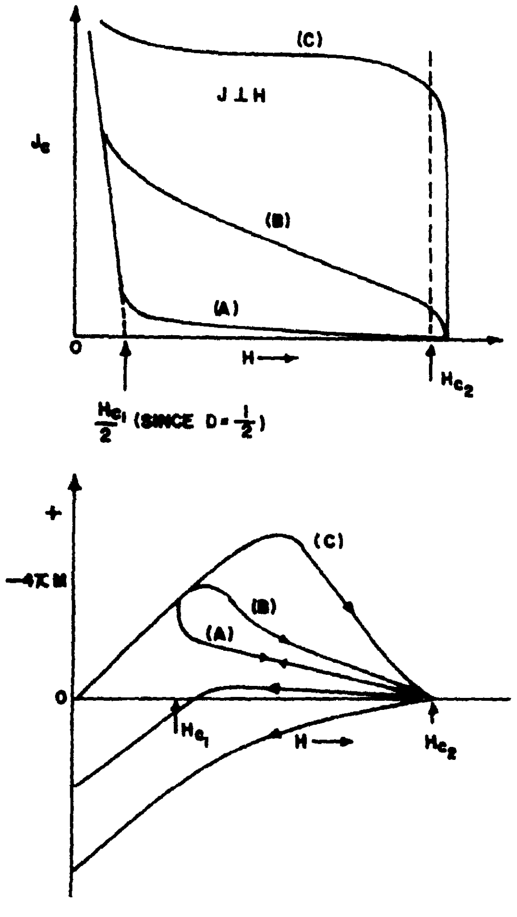

Fig. 6. Irreversible magnetization and Jc/H curves.

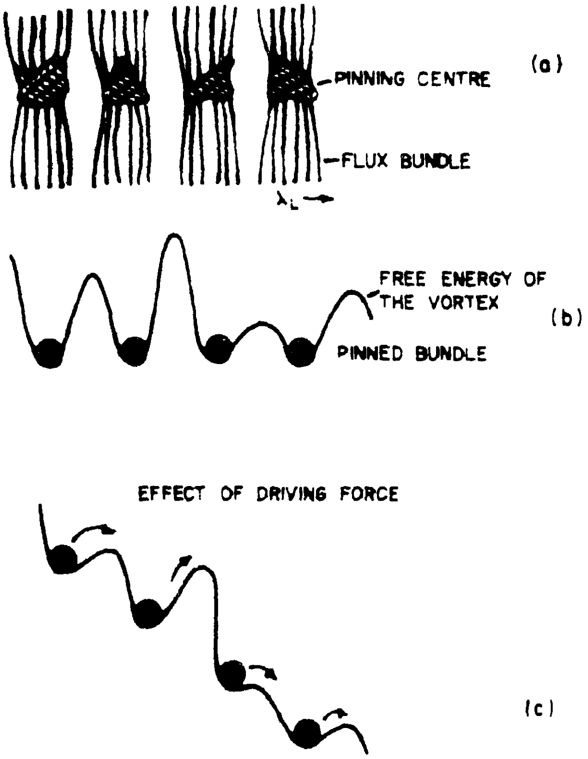

Fig. 7. Flux creep.

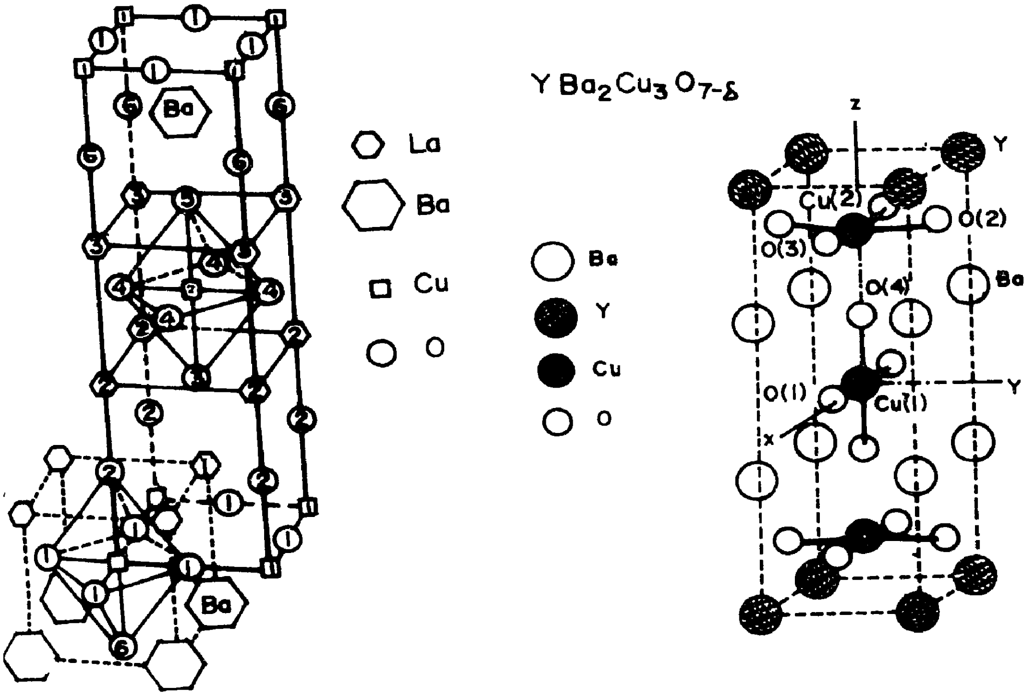

Fig. 8. Crystal structure of (a) La compound (214) and (b) Y compound (123).

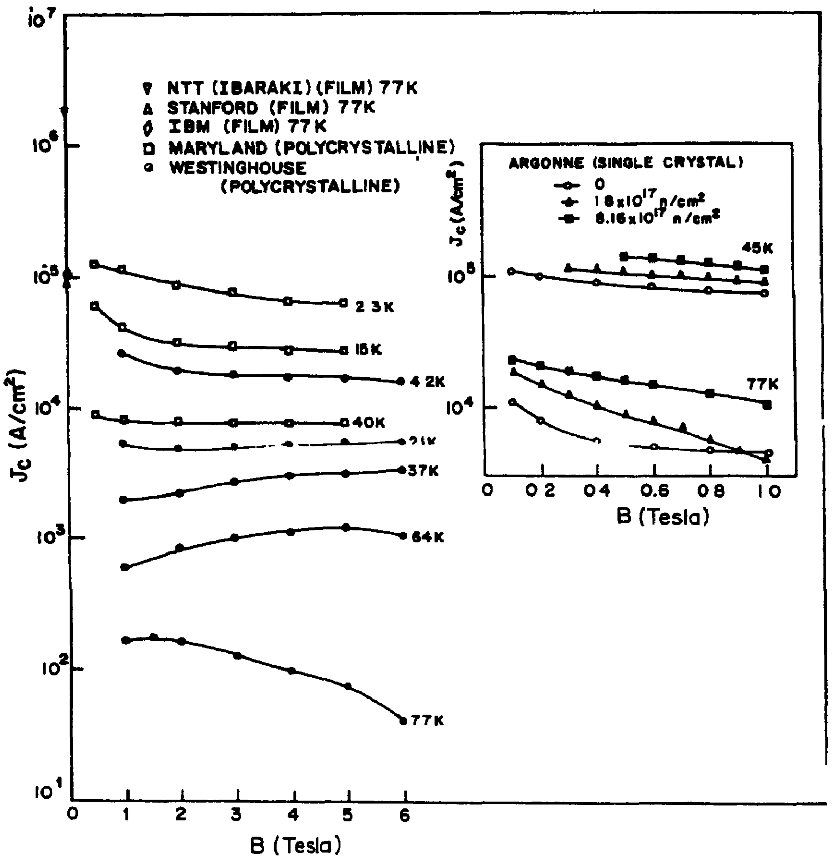

Fig. 9. Jc(B) data for polycrystalline and bulk single crystals of 123 compounds.

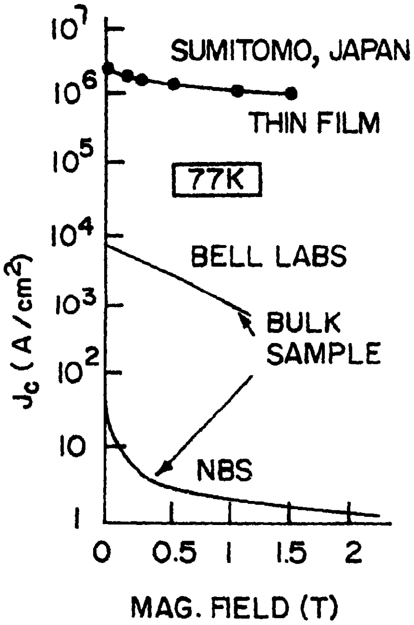

Fig. 10. Jc(B) data.

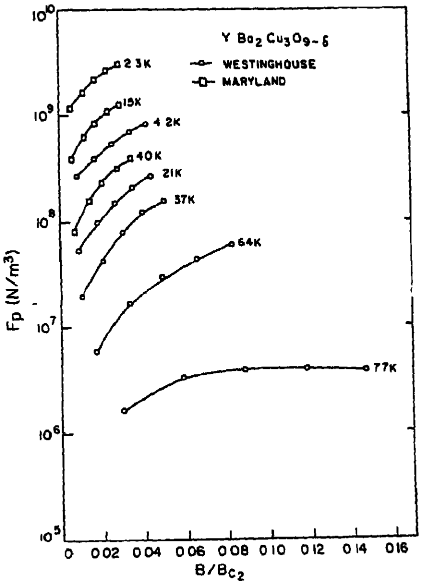

Fig. 11. Fp(B) curves.

Preparation techniques and properties of thin films of high temperature superconductors

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Abstract

In this nonspecialist overview we discuss the important parameters for the successful preparation and associated properties of thin films of $Y_1Ba_2Cu_3O_{6\,9}$ superconductors. We illustrate the principles by using the examples of monotarget, sequential and multitarget in-situ ion beam co-deposition techniques. We discuss magnetron sputtering and E-beam evaporation and comment on laser ablation, and molecular beam epitaxy. We then briefly discuss Bi- and Tl-film preparation, high critical currents and device related post-processing.

Introduction

The aim of this article is to give a very simplified review of the preparation techniques and properties of thin films of the high temperature superconductors presently under active investigation. We address this article at decision makers and non-specialists wishing to become familiar with the essential principles and problems associated with the preparation of thin films of these materials. To those interested in the detailed technical aspects of the various deposition techniques, we recommend some of the recent reviews and conference.proceedings listed in the references (1-15).

Elsewhere in this volume the reader can find detailed information on the materials problems inherent to the perovskite superconductors. In our review we assume that the reader has an elementary understanding of the chemical composition, crystallographic structure and anisotropy of these materials, $Y_1Ba_2Cu_3O_{6.9}$ in particular.

In the first section we explain some of the conditions needed to succeed in preparing $Y_1Ba_2Cu_3O_{6.9}$ superconducting thin films. We illustrate the main principles with the example of ion beam sputtering from a single composite target, sequential ion beam deposition and then by a new in-situ multi-target codeposition system. We then briefly discuss magnetron sputtering, E-beam evaporation, laser ablation and molecular beam epitaxy. We try to stress the advantages and shortcomings of each of these techniques. In the final section we comment on the advances in preparation of Bi- and Tl- thin film superconductors. We then discuss the problems of uniformity, critical currents and postprocessing needed to successfully produce certain (opto)electronic or Josephson devices from these materials.

Film preparation

To achieve reproducible preparation of superconducting thin films one has, at the very least, to control the following parameters:

1. The stoichiometry, i.e. the correct ratio between Y, Ba and Cu in $Y_1Ba_2Cu_3O_{69}$. One may still measure a superconducting transition in films in which the stoichiometry differ up to about 20% from the ideal "1:2:3" ratio, particularly in polycrystalline films of about one micron thickness. But, to achieve narrow resistive transitions and grow oriented epitaxial films suitable for device structures, the stoichiometry has to be within about 0.1%.

2. Assuming one has the orthohomic structure, one has to ensure sufficient presence of oxygen in the final film. For example, even if the metallic stoichiometry corresponds to "1:2:3" ratio, the film with only "O_{67}" would most likely exhibit zero resistance at about 60K, rather than at 90K for the O_{69} case.

3. To achieve thin film critical current densities in excess of 10^5 Acm^{-2} at 77K one has to achieve epitaxial growth with the c-axis perpendicular to the (100) $SrTiO_3$ substrate plane (6,11). The critical current densities of non-oriented and polycrystalline films are low and comparable with those achieved in most bulk ceramic samples.

4. For most optical measurements and device processing applications one has to ensure a very uniform film deposition rate over wafer size dimensions (at least several cm^2). At present even the best films do not satisfy this criterion.

Deposition techniques

Most of the techniques of film preparation can be divided into three main categories:

(a) **Monotarget Deposition:** Here the source of the film to be deposited is a single target of the bulk superconducting material. However, one cannot always assume that the target material stoichiometry is transferred to the growing film.

(b) **Sequential Deposition:** Here superconducting thin films are achieved by the sequential deposition of the cation components from separate targets followed by subsequent ex-situ post annealing in flowing oxygen.

(c) **Multitarget Co-deposition:** In this case, each elemental cation component is simultaneously deposited from separate targets. For $Y_1Ba_2Cu_3O_{6.9}$, three targets are needed, for BiSrCaCuO, four, etc. Exact film stoichiometry is achieved by adjusting the cation component flux rates.

To illustrate the underlying principles of different preparation categories we in turn now briefly describe ion beam examples of the above three categories. In subsequent section, we stress the differences and similarities of these with the other principle deposition methods for high T_c superconductors.

Monotarget deposition

In Figure 1 we present a schematic diagram of our monotarget ion beam apparatus (13). It consists of a high vacuum chamber (base pressure 10^{-7} Torr) into which is mounted a 2.5 inch diameter 1500 eV ion beam source, a water cooled target holder and an oxygen inlet tube directed at the heated substrate holder. An $Y_1Ba_2Cu_3O_{6.9}$ ceramic target, 50 mm diameter, 15 mm thick is used as the target. This was prepared by the standard procedure of sintering and calcinating the stoichiometric mixture of constituent oxide powders. Amorphous films were deposited on sapphire or (100) $SrTiO_3$ using the following typical sputtering parameters: Argon pressure 10^{-3} Torr, ion beam current 50 mA, beam voltage 1KeV. Typical deposition rates were one micron per hour. The as-sputtered films, deposited at substrate temperatures below 500°C, were always amorphous.

If subjected to a thermal anneal in an oxygen atmosphere, such films crystallise into the tetragonal phase (above 650°C), which transforms to the orthorhombic phase on cooling below 630°C. They then take up the necessary oxygen "O_7" at about 400°C. This somewhat over-simplified description is schematically illustrated in figure 2 which shows how the electrical resistivity changes during heating and cooling in an oxygen atmosphere. In figure 3 we show one of the numerous possible annealing procedures which usually transform amorphous, insulating films, containing the correct stoichiometric ratio of constituent metals to superconducting films. In figure 4 we show the relation between the substrate and the annealing temperature and the subsequent final state of the film.

Sequential deposition

By replacing the monotarget with a "carrousel" arrangement that holds several different metallic targets (Y, Ba, and Ag. for example), such as that illustrated in figure 1, one can fairly easily and economically evolve into a somewhat more versatile sequential deposition system. In this method one has to control precisely the rate of deposition. Y, Ba and Cu layers of different thickness are then suquentially deposited onto the substrate (see ref. 9 for details). After the anneal in oxygen (see figure 3), superconducting films are obtained. Our experience with this method has been somewhat negative. It is a long process to achieve the required individual layer thickness to ensure stoichiometry of the annealed film. One small advantage of sequential deposition over the monotarget case is that one can do some in-situ post-processing steps such as the deposition of an additional silver layer or some non-diffusive protection layer. One is of course faced with similar problems with monotarget deposition systems where it is an extremely slow iterative process to correct for stoichiometric deviations (due to sputter yield and sticking coefficient effects etc.) by changing the single target composition after each run.

Multi-component co-deposition

It is widely accepted that multi-component co-deposition is inherently much more flexible and controllable process particularly suited for the reproducible growth of high quality high-T_c superconducting thin films. It is therefore not surprising that most of the leading laboratories are currently working on several of the in-situ techniques we discussed in the fourth section.

Substrates

Before we describe the example of ion beam co-deposition, let us familiarize ourselves with most commonly used substrates (16-18). The crystallography and preparation of the substrate is of primary importance in determining the quality of the deposited film (16). So far the highest critical current densities and highest film uniformities have been achieved on commercially available (100) $SrTiO_3$ substrates. This is not entirely surprising as the lattice parameters of this substrate differs only by about 1% from that of $Y_1Ba_2Cu_3O_{6.9}$. Moreover, the (100) direction ensure crystal growth with c-axis oriented perpendicular to the substrate. This may be achieved in films of thickness up to about 250 nm provided that the deposition rates are low and the presence of abundant "nascent" or free atomic oxygen is achieved at the substrate. $LaGaO_3$, a substrate material recently discovered by IBM should enable even better results. The lattice mismatch of this material is only about 0.5% and it exhibits a more favourable thermal expansion coefficient and has superior mechanical properties than $SrTiO_3$.

Very good polycrystalline film results have been achieved with films deposited on yttrium stabilized zirconia (YSZ); this has a lattice mismatch of 30%. Very recently the Bellcore/Rutgers and SUNY Buffalo groups have successfully deposited thin superconducting films on Si susbtrates covered with a layer of ZrO_2. Such zirconia "buffers" will most likely play an important role in many technologically oriented efforts as it can be grown into complex heterostructures for devices.

Polycrystalline films can also be successfully deposited on silver layers or on sapphire substrates. In the latter case, the reported results vary dramatically between laboratories, but one can assert that sapphire can be used for most of the necessary preliminary technique optimisation work.

Good results were also reported on MgO (8% mismatch) and even on stainless steel substrates. Nevertheless, at present, most laboratories are using use (100) $SrTiO_3$ substrate at 400°C as a reference, other orientations such as (111) or (011) are usually used for depositions at substrate temperatures (T_s) above 400°C.

When the film deposition is carried out at $T_s > 650°C$ one encounters numerous problems with interdiffusion between $Y_1Ba_2Cu_3O_{6.9}$ and the substrate (17,18). This is the major problem wih sapphire substrates. There is no universally accepted solution to this problem. To reduce interdiffusion problems, one ideally would like to grow the film at the lowest possible substrate temperature which at present is between 450 and 500°C.

Advanced co-deposition techniques

In this section we briefly describe some of the most widely used co-deposition film preparation methods for the perovskite superconductors and try to emphasise their main advantages and some of the shortcomings. Of course, any attempt to compare different techniques is bound to be somewhat biased by the authors' preference. The reader should also study the original reports (1-15) to appreciate the merits of any particular technique.

Ion beam co-deposition

To our knowledge there are only a few groups at present actively pursuing research by ion beam sputtering (1). Only Sumitomo and E.P.F.L. are presently using wholly ion beam co-deposition techniques to grow films (13,19,20). At AT&T Bell laboratories $Y_1Ba_2Cu_3O_{6.9}$ films are prepared by a combination of ion beam co-deposition and thermal evaporation (14).

Figure 5 is a schematic illustration of the ion beam co-deposition system used in our laboratory at E.P.F.L. It was designed to deposit up to three materials simultaneously, and up to eight materials sequentially. It consists of a cylindrical vacuum chamber of a base pressure 10^{-7} Torr (without bakeout) equipped with four Kaufmann ion guns. Three of the ion guns are arranged in a triangular geometry approximately 15cm from the sputter targets. The beam extraction grids of each ion gun are arranged so that Ar^+ ion beam is focussed at each target which is angled at 45° to the incident ion beam. Each ion source has a three cm ion beam diameter and can produce ions of energy up to 1500eV at beam currents up to 70mA. The fourth Kaufmann ion gun, equipped with defocusing extraction grids, is positioned symmetrically within this triangle but facing the other three ion beam guns and the substrate. This fourth ion gun is modified to facilitate low energy (<50eV) oxygen ion bombardment of the growing $Y_1Ba_2Cu_3O_{6.9}$ film. The substrate carrier can be rotated and heated to 850°C. To further augment the supply of nascent oxygen to the growing film, a jet of oxygen is also provided at the substrate surface.

To attain the required stoichiometric control for epitaxial film growth, the deposition rates from each gun are indepently maintained by a continuous feedback control system using four independent quartz crystal monitors (20). The partial pressures of the process gases are maintained by four independently controlled mass flow controllers. Residual gas analysis is carried out by quadrupole mas spectrometer.

By using Kaufman ion guns, the Ar or Xe plasma ion source is confined inside each gun. The advantage of this is that each plasma is therefore outside the main vacuum chamber and well away from the substrate. One thereby avoids the problems of re-sputtering effects due to negative ion bombardment which are so prevalent in all of the other sputter techniques. Kaufman ion sources also offer very versatile facility of independent control of both the sputtering ion beam energy and sputtering ion flux.

Kaufman ion guns are typically run at pressures in the range 5×10^{-5} - 5×10^{-4} Torr. At these pressures one can assume line-of-sight dynamics which means that one can readily deposit patterned films in-situ by liftoff. As ion beam sputtering is a purely physical phenomenon it may be used to deposit all materials, whether insulating or not. The latest ion gun designs are modular in design and much simpler in construction than earlier models, these can be rapidly dismantled for cleaning purposes. Ion guns are now being manufactured with beam diameters in excess of six inches for which there is now considerable interest for covering very large areas by this technique.

An important characteristic of ion beam sources is that they can also be used for ion beam etching. This is of particular relevance to thin film of high-T_c superconductors as many groups have found that conventional wet etching with acid mixtures rapidly destroys any trace of supeconductivity. This problem is particularly serious in polycrystalline films. Ion beam etching, being anisotropic, is particularly well suited for etching fine line patterns such as those required for high-T_c SQUIDS (21). In addition to using photoresist as an etch mask, metal overlayers patterned by plasma etching may also be used as a mask during the ion beam etch stage. Such an in-situ ion beam etching capability is invaluable for pre-cleaning the substrates immediately prior to $Y_1Ba_2Cu_3O_{6.9}$ film deposition. One cannot, for instance, use magnetrons for etching. It is for this reason that so many magnetron systems nowdays include an extra ion beam gun for etching or precleaning the substrate prior to deposition.

Ion beam guns introduce the exciting possibility of simultaneous in-situ ion beam oxidation (see Table 1) of superconducting thin films as they are being deposited (20). As each sputtered atom has an equivalent thermal energy as an atom at several tens of thousand Kelvin, the oxidation can be carried out at relatively low temperatures. The benefit of this is that one can thereby avoid elevated substrate temperatures and some of the previously mentioned problem of substrate interdiffusion. Ion beam sputtering is already a well established method of routine deposition and etching of transparent, conducting and antireflecting films for optoelectronics applications. The technique is therefore well suited for research on novel (opto)electronic, possibly hybrid semi-conductor superconductor device structures and whole-wafer processed tunnel junction structures.

Magnetron sputtering

Of the co-deposition techniques presently being studied, most of the polycrystalline superconducting thin films to date have been grown by DC or RF magnetron sputtering (1,7,8,12). The reason for this is simply that these techniques are relatively simple, cheap and most widely available.

However, although so widespread, magnetron sputtering is not necessarily the easiest technique for preparation of high quality superconducting high-T_c films. As has already been discussed in this overview, to achieve epitaxy and superconductive transitions widths of less than about 1K, one needs extremely fine control of the relative composition of the growing film. This cannot easily be maintained by magnetron sputtering. The reason for this is that the plasmas, which provide the source of the sputtering Ar ions, are all in the same vacuum chamber. This plasma (and hence the Ar ion flux) is very dependent on the pressure inside the chamber, one cannot therefore independently control this for each magnetron. For similar reasons one cannot independently control the energy and flux of the sputtering ions by magnetron techniques.

Moreover, DC magnetrons do not allow one to continuously lower the total sputtered flux from each magnetron target by simply decreasing the high negative potential on the magnetron. If one does this, the plasma frequently simply dies. To ignite a magnetron one also has to backfill the whole vacuum chamber to relatively high pressures (10^{-2} Torr) and then slowly drop the pressure in an attempt to control the sputtered flux. This setting-up procedure has of course to be carried out with each magnetron independently and shuttered from the substrates. We have found that shutters near magnetrons often cause the plasma to die when they are removed.

With magnetrons the plasma is often within a few cm of the substrate. This has led to immense problems caused by the re-sputtering of the deposited films by negative oxygen ion bombardment. This problem is worsened in RF plasmas which cause oxygen molecules to dissociate and release negative oxygen ions. Due to the proximity of the substrate to the magnetron target, magnetron sputtered films do not offer good spatial uniformity over large areas. Perhaps most importantly DC magnetrons do not allow the possibility of sputtering from insulating targets. This is of particular relevance to high-T_c films as some of the highest quality co-deposited $Y_1Ba_2Cu_3O_{6.9}$ films have been grown using insulating BaF_2 as the source of Barium. Metallic Barium is particularly difficult to work with as it rapidly oxidizes to form crusts of hydroscopic (and toxic) BaO when exposed to air. This is always the case when loading substrates into the chamber, unless it is load-locked. Insulating targets may be however used with RF magnetrons but the RF noise generated by these systems is frequently incompatible with quartz crystal monitor feedback control systems and computers.

Despite some of these problems, magnetron sputtering will nevertheless remain one of the most widely used techniques. It is relatively cheap and reliable and one can use small targets that can easily be replaced. Moreover, it is relatively easy to find scientists and technicians familiar with the operations of these systems. This is not always the case with some of the other techniques like laser ablation or molecular beam epitaxy for example.

Electron beam co-evaporation

Several well known laboratories such as IBM, Stanford University, AT&T Bell Labs, NTT, Geneva and Cornel University are using electron beam thermal co-evaporation to produce superconducting films (2-6,15). Most likely reason for this is that this technique is relatively straightforward and clean and as everything is carried out under UHV conditions, the deposition rates are high. It is for this reason that co-evaporation has provided films with lowest contamination levels. Indeed some of the best superconducting films produced to-date have been deposited by this technique. Moreover, as these films are deposited by line of sight. this is ideal for liftoff patterning.

The principle disadvantage of technique is that it is not very flexible. One cannot change the deposition parameters, only the deposition rate. Evaporated films are deposited at a much lower energy than sputtered films and hence the depositing atoms have much lower surface mobility. For this reason, thin evaporated films are much more likely to be less continuous than sputtered films. As with magnetron sputtered films, the principle disadvantage of electron beam co-evaporation is its inherent lack of control. Furthermore one is still limited in the range of materials that can be evaporated. For example, several insulating refractory materials for which there is considerable interest as artificial deposited tunnel barrier for device applications (such as Y_2O_3) cannot easily be deposited by this technique.

Due to the very high melting point of the source material one has to be very careful in selecting the material of the containment vessel to avoid the melt reacting or interdiffusing with the container. At very high source temperatures required, heating effects due to radiation from the melt source are frequently observed. These effects are particularly damaging to optoelectronic films. As stated earlier, such films may be among the first semiconducting materials to be incorporated with high-T_c films in hybrid devices.

The spitting of droplets of molten metal is another frequent hazard encountered with electron beam evaporation, so the uniformity and control of the film thickness can be relatively poor. Finally, as it is the vapour pressure that determines the relative evaporation rate from each element, one cannot deposit alloy films from a single source that have the same composition as the alloy sources. E-beam evaporation and magnetron sputtering are discussed further and in some detail in refs. 5 & 15.

Laser ablation

Laser ablation of high temperature superconductors was first used by Bellcore group (10). Due to the apparent simplicity of this method this quickly became very fashionable technique despite the fact that most laboratories cannot deposit over areas larger than about one cm^2. Strictly speaking this technique should not be included among co-deposition techniques as, to the best of our knowledge, this has so far only been used for monotarget depositions.

For laser ablation one requires a pulsed excimer laser and a small ceramic pellet (typically about 1 cm in diameter) as a target held in a suitable substrate holder. Using the laser beam one deposits the pellet material directly onto the adjacent substrate. Recent reports suggest that it is beneficial to use an oxygen flow directed onto the substrate, or preferably reactive oxygen plasma. It is anticipated that oxygen ion beam assist techniques such as those described earlier will also be added to existing laser ablation systems in the near future. The SUNY-Buffalo group have succeeded in depositing superconducting thin films even with substrate temperatures below 500°C which is particularly well suited for the direct deposition on silicon, although a zirconia buffer substrate layer is nevertheless desirable.

The laser ablation process is not yet fully understood and it is not clear whether the "1:2:3" stoichiometry of the pellet is always "transferred" to the substrate. Further experimentation is needed to elucidate the role of various parameters like the geometry of the experimental arrangement. It is at present difficult to speculate as to what is the largest film area that can be deposited with high uniformity at a relatively low cost. It is quite probable that laser ablation will be added to one of the existing ion beam or E-beam systems so we might see some exciting processing advancements in the early nineties.

Molecular beam epitaxy

To our knowledge there are at least two major research efforts on the growth of high-T_c thin film superconductors by molecular beam epitaxy (MBE). These groups are the Stanford/Varian collaboration (U.S.A.) and Rieber/Thomson collaboration (France) (15,22). In the context of growth of artificial structures of GaAs/AlGaAs semiconductors it is well established that the ultra high vacuum of the MBE chamber (10^{-11} Torr) and very low deposition rates (only few angstrom per second), achieved using the fine thermal beam from a Knudsen cell, give an impressive control of the epitaxial growth down to atomic monolayer.

However, at present, it is difficult to see any real advantage for the deposition of thin films of high temperature superconductors where one needs a considerable oxygen partial pressure in the growth area close to the substrate (see Table 1). Partial oxygen pressure reported for MBE are either insufficient for in-situ growth (10^{-7} to 10^{-4} Torr) or impracticable to use within the ultra high vacuum chamber of the conventional MBE system (10^{-11} Torr). The fine features of MBE technique would probably be of benefit only if one could achieve controlled in-situ growth of individual layers. In that case one might be able to engineer even novel superconducting structures on the atomic level. However, at present this technique is too expensive for most laboratories and does not show any clear advantage over the other methods discussed earlier.

Concluding remarks

Following the discovery of Bi- and Tl- superconducting oxides, several laboratories have successfully produced thin films by some of the above techniques and reported critical current densities of about 10^6 Acm^{-2} at 100K for some of these films. However, it is well known that thallium is a highly toxic element and great caution is necessary when one handles oxides of this element or cleans the evaporation system after several depositions.

Most Bi- films, including the single crystals and ceramics, seem to contain at least two phases and the critical current appears to be very sensitive to external or local magnetic field. Contrary to $Y_1Ba_2Cu_3O_{6.9}$ reports on postprocessing, reports of patterning Bi-films are at present somewhat discouraging. According to the experience of the Philips group with $Y_1Ba_2Cu_3O_{6.9}$ (2,4), the primary requirement for successful patterning is that the films are uniformly deposited and practically epitaxial. In polycrystalline films one quickly degrades the superconducting properties with every processing step and consequently the critical temperature and current density rapidly decrease.

It takes about a year for a well organized laboratory to master the preparation of thin films of a given chemical composition, so it is not surprising that in the autumn of 1988 $Y_1Ba_2Cu_3O_{6.9}$ thin films still appear to be of somewhat better overall quality than the Tl- or Bi- films. That also implicitly explains better the generally higher quality of research reports on device oriented processing of $Y_1Ba_2Cu_3O_{6.9}$. However, one should emphasise that even the most uniform, epitaxial $Y_1Ba_2Cu_3O_{6.9}$ films seem to be of sufficiently high quality only within relatively small areas. It will probably take another year or two until even the largest laboratories achieve perfection in processing large areas (several cm^2) of uniform, truly epitaxial films that will lead to rapid technological developments particularly in the field of whole-wafer type tunnel junction structures and high critical current interconnects.

In conclusion we note that within the past two years we have witnessed major advancements in the preparation of thin films of high temperature superconductors. Superconducting thin films of $Y_1Ba_2Cu_3O_{6.9}$ have been produced by virtually any known technique. It is probably true to state that any technique should produce good films if adequate know-how and persistent research efforts are combined. But for its inherent controllability and flexibility, we believe that ion beam co-deposition presently offers a very viable route for highly stoichiometric textured and possibly epitaxial thin films of high-T_c superconductors.

In this simple overview we have also tried to emphasize what we believe to be main strengths of the different methods: magnetron sputtering as a relatively cheap, simple and widely available technique, E-beam for clean evaporation of thin films primarily for fundamental research, and ion beam sputter co-deposition for its flexibility and stoichiometric control for research and development of novel heterostructures for (opto)electronic devices. Laser ablation is a promising method for a future preparation/processing technology. Finally molecular beam epitaxy is an experimental technique that some day might enable us a very fine control of the layer by layer growth of these fascinating new materials.

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Table 1. Parameters of in-situ growth techniques in several laboratories

Laboratory	**Technique/Source**	**Oxygen incorporation**	**O_2 pressure at substrate surface**	**T_{sub}/°C (Torr)**
Kyoto University	thermal evaporation Y,Ba,Cu metals	O_2-flow with RF plasma activation	10^{-2}~10^{-1}	550~650
Bell Core	pulsed excimer laser/sintered pellet	ambient	10^{-1}	650
Stanford	thermal evaporation Y,Ba,Cu metals	atomic oxygen from microwave discharge	$3x10^{15}$*	~600
AT&T Bell Labs	thermal evaporation Y,Ba,Cu metals	reactive oxygen by Microwave plasma	$6x10^{15}$*	550
NTT	thermal evaporation Y,Cu, metals BaF_2	ECR ion beam	10^{15}*	600
Siemens	pulsed excimer laser, sintered pellet	ambient	10^{-1}	720-780
Ecole Poly-technique Lausanne	ion beam sputtering codeposition Y,Cu,BaF_2	ion beam oxygen assist & O_2 flow	~10^{-2}-10^{-3}	650-700 ao

*the flux of the activated oxygen at the substrate/cm^2 sec.

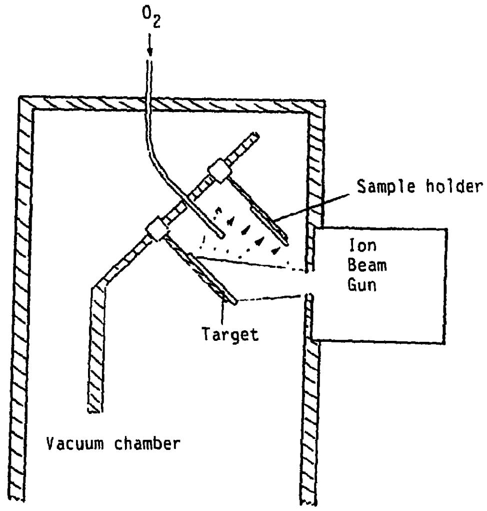

Fig. 1. Schematic presentation of a simple monotarget ion beam sputtering system

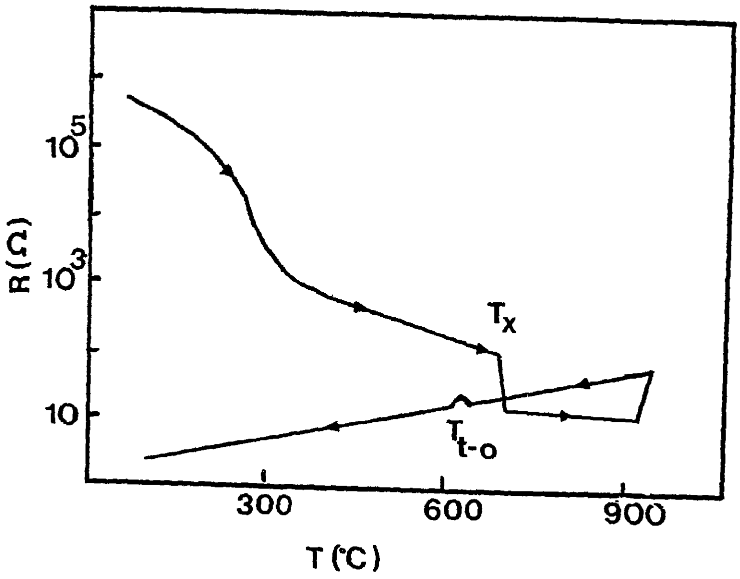

Fig. 2. Temperature variation of electrical resistivity of an initially amorphous film during annealing in oxygen;note characteristic temperatures of crystallisation (T_x) and tetra-orthorhombic transformation ($T_{t\text{-}o}$).

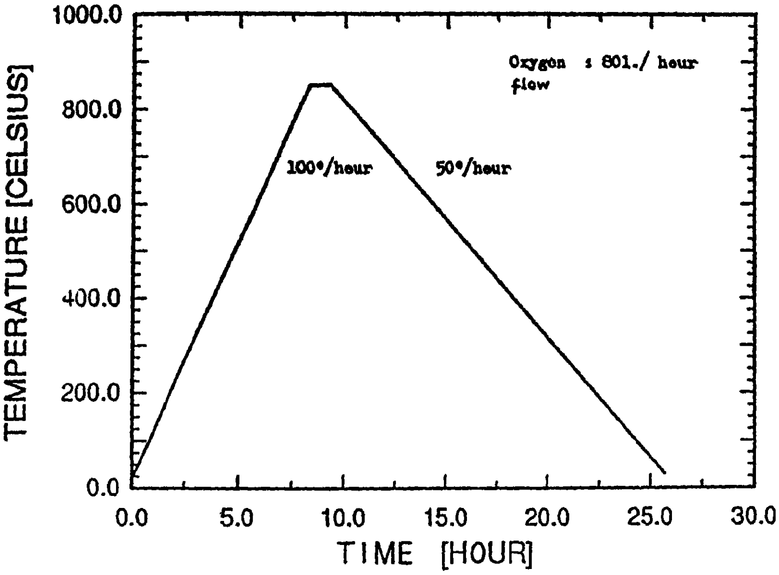

Fig. 3. Typical annealing procedure for as deposited films

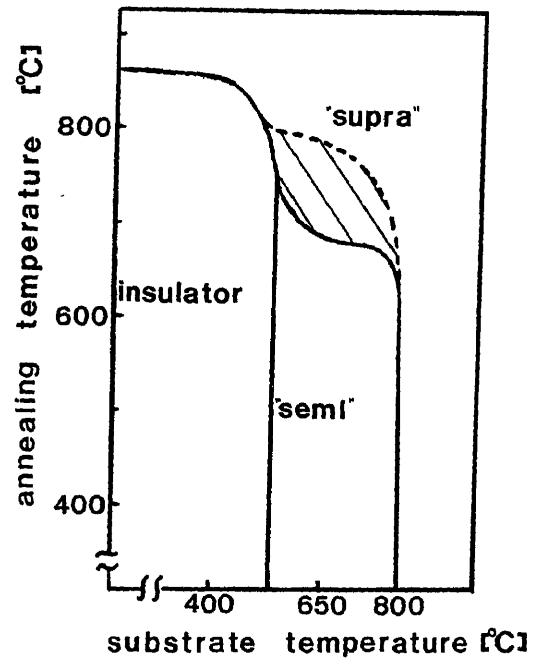

Fig. 4. Illustration of the relation between the substrate temperature, annealing temperature and the resulting film.

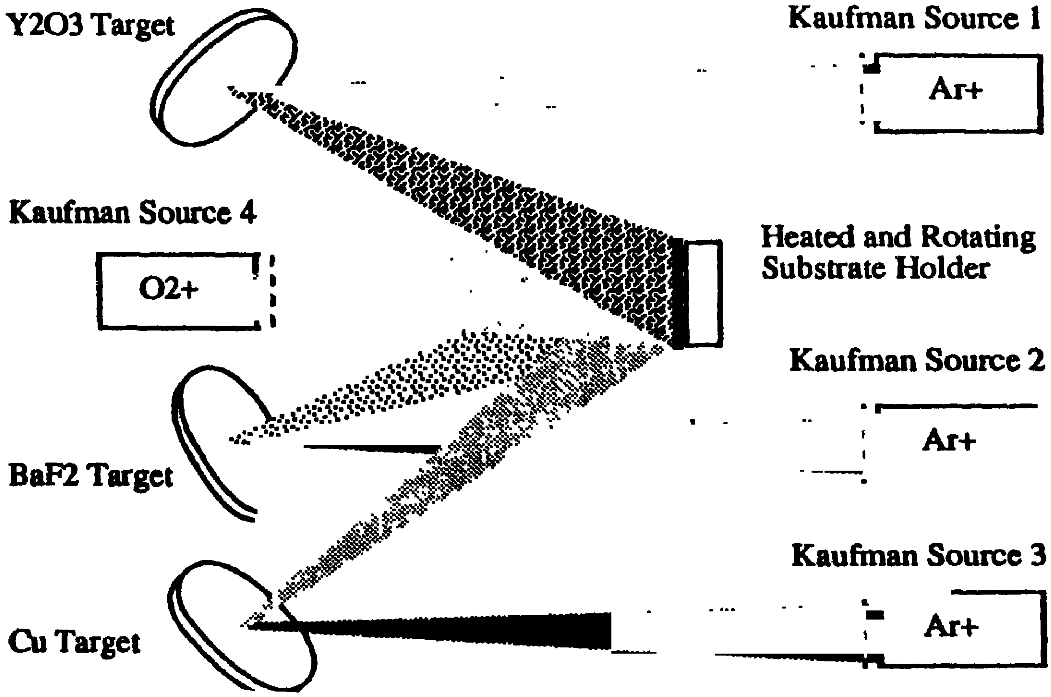

Fig. 5. Schematic presentation of the novel 4 ion beam source co-deposition system (20). (Courtesy Commonwealth Scientific Corporation, Alexandria, USA).

Squid magnetometers made from high temperature superconductors

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Abstract

RF and DC SQUIDs are superconducting sensors of magnetic field of unparalleled sensitivity. Although hitherto they have been restricted to operation at liquid helium temperatures, they can now be made from high temperature superconductors and operated at liquid nitrogen temperatures, with at least some loss in performance. The principles of operation, present applications and desired technological developments are sketched in this introductory paper, following which the potential and present performance of such devices is discussed. Already useful devices have been demonstrated at liquid nitrogen temperatures. Although some of the technical problems are considerable, progress is being made towards devices that will serve in all but the most taxing applications, where the lowest temperatures will remain mandatory.

Introduction

The Superconducting Quantum Interference Device or SQUID is a magnetic field sensor that can be made from superconducting material. The sensitivity of the best SQUIDs made from low temperature superconductors and operated at 4.2 Kelvin approaches the highest allowed by the physical laws of measurement. The applications of such sensitivity range widely, from use in fundamental research laboratories (including extensive use in research on high temperature superconductors) to geological prospecting and medical investigations. Considerable operational convenience and economy can possibly be obtained by using SQUIDs that operate at the much more accessible temperature of liquid nitrogen, 77 Kelvin. It is only since the discovery of high temperature superconductors that this has been possible. Apart from a slight worsening of the performance of SQUIDs brought about directly by the increased operating temperature, differences in kind between the metallic low temperature superconductors and the metal oxide high temperature superconductors bring their own difficulties in the fabrication and successful operation of SQUIDs. This introductory paper summarizes some of the ways that have been tried to overcome these difficulties and the present and possible future performance of high temperature SQUIDs. Attention is drawn at this point to some important general review articles on SQUIDs (1,2) and other superconducting devices (2).

A SQUID is essentially a superconducting ring, usually of size 1mm or smaller, that is interrupted by one or two weak links where the superconductivity is weakened to such an extent that the maximum supercurrent that can be supported is much reduced. From this and some conventional electronic apparatus can be made a magnetic field sensor of unparalleled sensitivity. The existence of superconductors that are superconducting at liquid nitrogen temperature is not in doubt (although some problems remain because they are not such simple entities as low temperature superconductors). Of more concern is the control with which suitable weak links can be fabricated. We therefore begin there.

Weak links

In addition to the existence of a supercurrent and consequent absence of electrical resistance, another most important property of superconductors is the possibility of the supercurrent traversing a region in which the superconductor has been in some sense weakened, or even replaced completely by a non-conducting barrier. Such a barrier is known as a weak link. Practical methods for making weak links in conventional superconductors are well established. They include (a) the fabrication of a sandwich structure consisting of a layer of superconducting metal, a thin (perhaps 2.5 nm) layer of an insulator and a second layer of superconductor, forming what is known as a Josephson tunnel junction (Figure 1a); (b) the removal of all but a fine slither of superconductor connecting two larger areas of superconductor, the whole being again in the form of a thin film of superconductor supported on an insulating substrate, forming a Dayem microbridge (figure 1b); and (c) the bringing together of a pointed (and possibly oxidized) superconducting screw and a superconducting anvil to form a point contact, whose microscopic operation may well be the same as that of the tunnel junction or the microbridge (figure 1c).

In weak links, as in unweakened pieces of superconductor, current is carried by pairs of electrons called Cooper pairs. While classical physics would forbid their travel through an insulating region in which they have no business to exist, quantum physics allows such travel by the picturesquely named process of tunnelling. For noticeable tunnelling to occur, it is necessary that the quantum mechanical wavefunction describing a Cooper pair in one piece of superconductor has some significant overlap with the second piece of superconductor. The "size" of the wavefunction is determined by the coherence length of the cooper pairs. The coherence length is of considerable importance in the fabrication of weak links because it sets the approximate length of weakened path that is required to form a weak link. In conventional low temperature superconductors this length is around 100 nm,setting a scale of length that can be achieved in the manufacture of weak links by the photolithographic techniques pioneered by the semiconductor industry. In high temperature superconductors such as YBCO however, the coherence length is about 1 nm, setting a much more challenging (and as yet unsolved) fabrication problem: it should be remembered that the spacing between individual atoms in the YBCO structure is only about 0.2 nm(3).

Fabrication of devices and weak links in high temperature superconductors

The ideal state of the manufacturing art would be the ability to lay down tracks of superconductor, forming tracks of arbitrary shape whose width and spacing were a few microns and to introduce insulating layers of thickness such as to form tunnel junctions between these tracks. Such technology exists in a highly developed form for conventional low temperature superconductors, being based on thin-film vapour deposition and photolithographic techniques.

A technology of comparable sophistication does not yet exist for high temperature superconductors. The chemical nature of these oxide superconductors prevents a simple borrowing of the existing technology. The oxide superconductors rely for their superconductivity on a precisely controlled mixture of several elements, which is chemically and thermally quite unstable and easily contaminated. However, many attempts to fabricate useful structures have been at least partially successful.

The crudest high temperature superconductor system containing weak links was shown to be simply a lump of sintered superconducting material, wherein the granular nature of the material itself provides the required weakening of the superconductivity (4), probably at the interfaces between grains. SQUID behaviour (5) and the nonlinear properties associated with Josephson junctions (6) have been demonstrated in such systems.

Several workers have capitalized on this property of the granular material by mechanically narrowing the superconductor to about 0.1 mm in the region where a weak link is wanted, starting with either a three dimensional piece of sintered superconductor (7) or a two dimensional polycrystalline film (8).

Another successful approach been to produce a crack in the superconductor by bending (9) or stretching (10), and presumably then to rely on conduction through a remanent connection between the sides of the crack. In the case where reliance is placed on the granular material, there is little control over the strength of, number of, or area enclosed by the weak links so formed; in the crack junction case an important problem is that of stability of the junction, especially during warming and cooling cycles.

A closer approach to the technology in use with low temperature superconductors promises better control and greater stability (11). In this case a YBCO film made by deposition of the metallic elements and subsequent annealing in oxygen was patterned to form a DC SQUID by ion implanting oxygen or arsenic, a process which turns the superconductor first normal and then insulating. The pattern of superconductor left intact was defined by the shape of a vacuum deposited gold mask which was itself patterned by conventional techniques and removed by ion milling. The weak links were still however formed as a result of the granular nature of the material itself; their nature and the effect of the patterning process reduced the effectiveness of the SQUID at temperatures above 40 K, the device degenerating completely above 70 K.

SQUIDs

SQUIDs, or Superconducting Quantum Interference Devices are devices that rely fundamentally on the basic property of superconductors, that the electrons carrying the supercurrent are described collectively by a single quantum mechanical wavefunction, to give a device that is essentially a magnetic flux - to - voltage transducer. They owe their special place in the field of measuring instruments to their exceedingly high sensitivity, and correspondingly small noise. SQUIDs made from low temperature superconductors have been made whose sensitivity approaches the highest that is allowed, even in principle, by the physics of measurement (12). There are many uses to which such sensitivities can be put in measuring instruments.

An obvious set of applications are those in geophysics, where the magnetic field is of primary interest. SQUIDS are used to survey the ground in the search for oil and ore deposits. The study of gradients in the earth's magnetic field is particularly important and is an application to which SQUIDs are well suited: a suitable configuration of SQUID and superconducting search coil or flux transformer is directly sensitive to gradients of the field. Magnetotellurics makes use of naturally occurring fluctuations in the electric field and the resulting electric currents flowing in the ground to deduce the electrical conductivity of the ground; the electric currents are detected through the magnetic fields that they produce. Paleomagnetism is the study of the natural remanent magnetic field of rock samples; with its laboratory companion rock magnetism it provides information on the history of the individual rock and its place in the geological history of the earth.

A rapidly developing field in which the high sensitivity of SQUID magnetometers is put to use is that of biomagnetism. In addition to being able to study magnetic contaminants in the body, it is possible to study the magnetic fields produced by electric currents flowing in body tissues. These include the skeletal muscles, heart and brain. In neuromagnetism particularly, there can be considerable benefit from SQUID measurements of the magnetic field as opposed to, say, electroencephalography. The electromagnetic activity of the brain is small, and the electric field is distorted by the skull, making the localization of sites of activity by electrical means difficult. The magnetic field is comparatively undistorted, and it has proved possible to locate and study the activity stimulated by aural signals and that present spontaneously in subjects with epilepsy.

In magnetic instrumentation, SQUIDs are used to provide sensitive magnetic susceptibility measurements on weakly magnetic materials over a wide range of ambient conditions, and are used extensively in research on superconducting materials. Other laboratory applications include the measurement of extremely small currents and voltages, by the use of appropriate resistors to produce currents from voltages and inductances to produce magnetic flux from currents.

Although traditionally SQUIDs have been used to measure low frequency magnetic fields - indeed, it in this regime that they have a great advantage over other magnetic field sensors - SQUID devices have also been made that respond at radio frequencies (not to be confused with ordinary "radio frequency" SQUIDs that, in fact, respond only to magnetic signals in the audio frequency range and below). Such devices have application in nuclear magnetic resonance analytical techniques, and other possibilities in the detection of radio frequency radiation.

RF and DC SQUIDs

For mainly historical reasons, the two fundamental types of SQUID are known as Radio Frequency and Direct Current SQUIDs. Both kinds of SQUID comprise an open area bounded by a ring of superconductor, ranging is size from 1mm down to a few μm. The difference is that in an RF SQUID the ring is interrupted by one weak link and in a DC SQUID it is interrupted by two. The detailed mechanisms of operation of these two devices (13) are not discussed here, but the principles of flux measurement are as follows: In each case some measurable property of the SQUID is dependent on the flux passing through the open area ("hole") in a periodic fashion. In the case of the RF SQUID the parameter is the damping of a radio frequency tuned circuit magnetically coupled to the hole; in the case of the DC SQUID it is the voltage developed between the two limbs of the ring of superconductor when a fixed current is passed from one to the other through the weak links. The period of the dependence is a magnetic flux equal to the quantum of magnetic flux, $\emptyset_0 = h/2e = 2 \times 10^{-15}$ Wb passing through the hole. Clearly, one could obtain quite a high sensitivity to magnetic field simply by counting periods of the changing parameter as the field changed. This is rarely done in practice. Instead an electronic feedback circuit is used to sense any variation in the parameter and to feed back into a coil near the hole a current of the correct size to nullify the change of flux in the hole caused by the variation of the external field to be measured. A measurement of this current by conventional techniques then provides a measure of the change in external field. Since the flux in the hole is actively maintained at a constant value, the arrangement is referred to as a flux-locked-loop. It has the benefit of giving a sensitivity determined by the noise in the system rather than by the larger intrinsic period of the SQUID. It is worth remarking that because of the periodic property, a SQUID does not provide information about the size of a static field, but only about variations in field, unless resort is made to techniques involving bodily motion of the SQUID.

In low temperature superconductivity, the RF SQUID was brought to a high state of development, and was available commercially, some years before the DC SQUID. This was partly because fabrication of the RF SQUID was easier, requiring only one, rather than two well-matched weak links. Subsequently the potentially much higher sensitivity available from the DC SQUID and the development of thin-film fabrication techniques has spurred the development and commercial availability of DC SQUIDs of increasing sensitivity. This has been true to a small extent in high temperature superconductors, but workers have been keen to devise thin-film techniques and exploit the potential advantages of DC SQUIDs.

Flux transformers and gradiometers

A SQUID is sensitive to the net magnetic flux passing through its hole, but rarely in fact is the SQUID simply exposed to the magnetic field to be measured. Usually the SQUID is magnetically shielded and a sample of the field to be measured is conveyed to the hole by means of a flux transformer, which is a continuous loop of superconducting wire or track formed into two coils. One coil is placed inside or adjacent to the hole in the SQUID and the other "pickup" coil, which is electrically in series with the first, is placed in the field to be measured. The mechanism of operation is simple: inside the closed superconducting circuit consisting of both coils the total magnetic flux must remain constant, therefore if the pickup coil is exposed to a field that increases the flux inside it, a corresponding decrease will occur in the flux in the coil in the SQUID. The advantages obtained are large and twofold. First, there is a high degree of flexibility in the geometrical arrangement and inductance of the pickup coil, while the coil inside the SQUID can maintain a high degree of magnetic coupling to the SQUID; and secondly the pickup coil can be wound so as to form a magnetic gradiometer. An ideal first order gradiometer is insensitive to the magnetic field, but is sensitive to a first spatial differential of the field i.e. the field gradient. A second order gradiometer is sensitive only to the second derivative of the field; this and higher order gradiometers can be fabricated by various winding schemes for the pickup coil (Figure 2a). Equivalent schemes are available in some cases for the planar structures obtainable by thin and thick film processes (Figure 2b). Apart from the direct measurement of the field gradient thus provided, the advantage of a gradiometer is that of interference rejection. At the magnetic signal levels at which SQUIDs are used, the effect of ambient magnetic noise can be a major problem being, for example, up to a million times larger than certain neurological signals in an urban environment. If it can be arranged that the sources of noise are further away from the pickup coil than the source of wanted signals, then since the higher derivatives of field decay rapidly with distance from the source, the gradiometer will sense only the nearby, wanted, signal while the nearly-uniform field of much larger magnitude from distant sources will be ignored. Often magnetically shielded enclosures and superconducting shields are used in addition, but with high order gradiometers this is not always necessary.

In order to make flux transformers and gradiometers from high temperature superconductors one requires either a thin wire that can be made into a continuously superconducting loop or a technique for making multi-layered two dimensional structures. Neither of these requirements is trivial, but both are under investigation (14).

Limitations on the performance of high temperature SQUIDs

It is inevitable that a higher operating temperature will result in a larger minimum intrinsic noise in any measuring system, since the temperature characterizes the size of random fluctuations. There are several ways of describing the noise level of a SQUID. The most direct is in terms of the flux noise in the hole of the SQUID, which is normally quoted in units of flux quanta per root hertz. In a magnetometer, of more concern is the noise in terms of magnetic field at the pickup coil of the flux transformer, often expressed in nT per root hertz. A third quantity that can be used to describe the noise level independent of geometrical factors is the energy of the flux noise per hertz, which is the square of the flux noise divided by twice the inductance of the SQUID. This last quantity has units of J/Hz, and is often given in terms of Planck's constant, h = $6.6\mathrm{x}10^{-34}$ J/Hz or h = h/2π = 10^{-34} J/Hz. Quantum mechanical zero-point fluctuations set a lower theoretical limit of about h on the noise energy. In all cases the units imply a bandwidth of 1 Hz in the noise measurement, and, if given without qualification it is implied that the noise is white, that is, the same size at all frequencies. In practice, at low enough frequencies the noise level rises with decreasing frequency and it is this 1/f or flicker noise that determines the sensitivity at low frequencies.

Research on low temperature DC SQUIDs has produced devices with noise energies as low as a few h to a few hundred h, the latter corresponding to about $10^{-6}\ \phi_0/\sqrt{\mathrm{Hz}}$. Commercially available DC SQUIDs are in the order of 10^4 h and RF SQUIDs about 10^6 h. Estimates (2,15) of the least degradation of these figures that can be expected on raising the operating temperature from 4.2 K to 77K lead to a rise in noise proportional to the rise in temperature for the DC SQUID, and proportional to the 4/3 power of the temperature for the RF SQUID; in both cases a factor of about 20. Extra noise is also certain to be found because of imperfect superconductors and weak links. It is important to consider whether low frequency (1/f) noise will make things worse. In low temperature superconductors such noise arises from trapping of electrons in the weak links and from the motion of flux lines penetrating the bulk superconductor. It is possible to keep both within manageable proportions by careful control of the superconducting materials and the fabrication process. However, an increase in temperature often leads to an increase in this kind of noise, and combined with the poor control presently available over materials and weak links in high temperature devices and the multiplicity of incidental weak links within the bulk of the material, the effect of 1/f noise in high temperature SQUIDs might be very important.

Present high temperature RF SQUIDs have attained at 79 K a white noise of about $5\mathrm{x}10^{-4}\ \phi_0/\sqrt{\mathrm{Hz}}$, with a 1/f component of equal magnitude at 10 Hz, rising steadily below that frequency (7). High temperature DC SQUIDs have attained $10^{-5}\ \phi_0/\sqrt{\mathrm{Hz}}$ at 40 K, with again a substantial 1/f contribution (16). Hopes for improving the performance of these devices rest on gaining an understanding of the cause of their excess noise and obtaining control over flux motion and trapping sites in the materials. Already their performance is competitive with fluxgate magnetometers.

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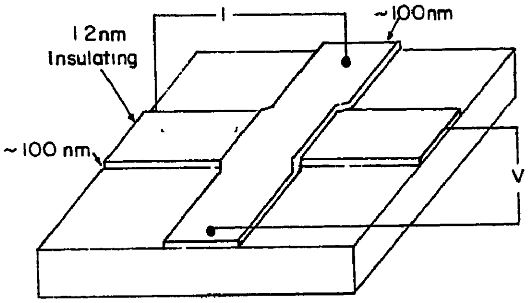

Fig. 1a. Superconductor-insulator-superconductor Josephson tunnel junction. *(after Falco and Schuller)*

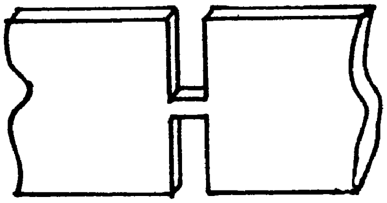

Fig. 1b. Dayem microbr

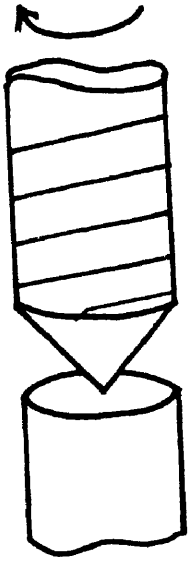

Fig. 1c. Point contact

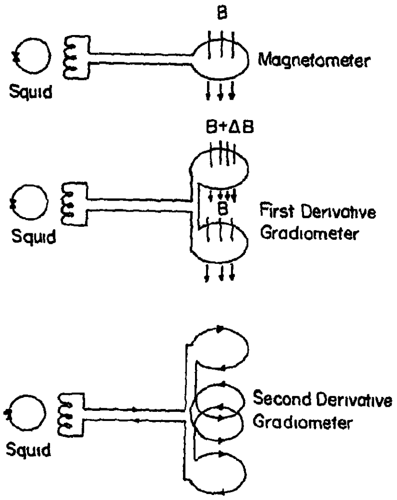

Fig. 2a. Gradiometer flux transformers made from wire. *(after Falco and Schuller)*

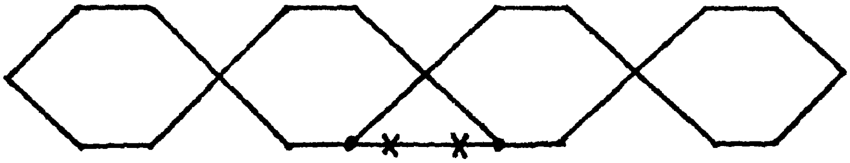

Fig. 2b. d^2Hz/dx^2 thin film gradiometer tracks that cross, but do not connect *(after Clarke 1986)*